A Technical Assessment of the Reactivity of Saskatchewan Lignite Coals as They Relate to Gasification Processes

FINAL REPORT

by

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Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, Canada

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EXECUTIVE SUMMARY

The gasification reactivity of Saskatchewan lignites has been examined during four Phases of this program. In the present Phase (V) an APL computer language program has been developed to reduce all data to a common basis for further analysis. Through this analysis, an accurate method has been developed and tested for the rapid determination of gasification reactivity parameters of various lignite samples under diverse reaction conditions. The kinetic expression developed is:

$$k/k^* = 1.16 + 1.24\ (Y) \times 10^3$$

where Y is the concentration of calcium or sodium in moles per gram of fixed carbon in the lignite, and k, k^* are the apparent rate constants for the cation-enriched and acid-washed samples, respectively.

The equation permits prediction of the extent of the char/steam reaction, and, when combined with other information such as air flowrates, etc., it allows the design of a gasification reactor based on chemical reaction engineering principles.

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INTRODUCTION

The controlling step in coal utilization processes such as gasification, combustion, liquefaction and pyrolysis is the heterogeneous kinetics of char gasification or combustion. Thus, for efficient coal utilization, it is of paramount importance that research be carried out and information be gathered on the reactivity of coal char.

Through a Lignite Reactivity program, Saskatchewan Power Corporation has examined in great detail many aspects of the air or air/steam gasification of Saskatchewan lignite chars. Research has centred on the following: the gasification potential of lignite in relation to its petrographic analysis; the optimization of process variables; the environmental pollution potential of effluent streams from a lignite gasification reactor; and, the catalytic potential of coal minerals (sodium and calcium) in steam gasification of lignite char.

Specific conclusions reached during the first four Phases of this program are as follows:

Phase I It was determined that Estevan lignite could be gasified with an efficiency of up to 99 percent using steam/air mixtures. Methane production increased with increasing reaction pressure. It was postulated that the reactivity of lignite

char varied as the ratio (structured huminite + liptinite)/(unstructured + inert macerals).

Phase II The heating value of the product gas increases with increasing pressure, up to 4MPa. At this pressure, heating values as high as 14 MJ/m^3 have been obtained. The overall rate of reaction generally decreased with increasing pressure. Estevan coal produced gases with marginally higher heating values than did Coronach coal.

Phase III More than 90 percent of all metals entering the reactor with the coal remain with the gasifier residue. Trace elements which leave with the liquid condensate are mostly below the allowable concentration, and are similar to those observed for large-scale, fixed-bed gasifiers.

Phase IV The exchangeable cations Na^+ and Ca^{++}, inherently present in untreated lignites as carboxyl salts, show a pronounced catalytic effect on the rate of gasification of lignite chars by steam or steam/air. The catalytic effect is similar for both cations, when calculated on a mole/g fixed carbon basis.

Throughout the experimental work of the past four Phases, data have been acquired on all facets of the gasification reactivity question. In Phase V this information has been correlated using in-house computer programs (See Appendix) and theoretical treatments proposed by others, to arrive at a unified approach to reactivity. The range of conditions under which testing was carried out was, we feel, wide enough to encompass the operation of most commercially run gasifiers. Results obtained on the bench-scale gasifier correlated well with available commercial data. We are confident, therefore, that the design data generated in this Phase of the study are relevant to commercial design. Enough information and procedures are contained herein for a potential coal gasifier operator to conduct sensitivity and feasibility studies to determine the appropriateness of the economics of entering the lignite gasification market.

BACKGROUND

Of the almost 64 billion tonnes of coal making up Canada's measured and indicated coal resources, one quarter is classified as mineable using current technology, and only 9 percent (5.9 billion tonnes) is considered recoverable (mineable with current technology at current market prices). Table 1 is a breakdown of Canadian coal resources, reserves and production by area, rank and mining method.

Lignite Reserves

An examination of Table 1 reveals some surprising statistics. While lignite constitutes 36 percent of Canada's recoverable coal reserves, its production in 1978— 5 million tonnes— accounted for only 14 percent of coal production across Canada. Lignite exists in British Columbia, the Yukon, Ontario and Saskatchewan (See Table 1 and Figure 1); however, Saskatchewan is the only Canadian lignite producer, and currently uses more coal in its primary energy balance than any other province (EMR, 1980). Almost all of this coal is used for electrical generation — over 90 percent — by the provincial utilities.

TABLE 1. CANADIAN COAL RESOURCES, RESERVES AND PRODUCTION (1978), BY AREA, RANK AND MINING METHOD (EMR, 1980)

Area	Rank	Resources	Reserves	Run-of-Mine Production in 1978
		(Million tonnes)		
British Columbia and Yukon	Bituminous	17,180	955	12.256
	Lignite	1,936	397	—
Alberta	Bituminous	9,300	530	7.408
	Sub-bituminous	30,000	2,182	8.310
Saskatchewan	Lignite	4,180	1,720	5.058
Ontario	Lignite	218	—	—
New Brunswick	Bituminous	48	33	0.315
Nova Scotia	Bituminous	766	89	2.894

Figure 1. MAJOR COALFIELDS OF CANADA
(Coal Association of Canada)

To increase lignite's share of the market, a large hurdle must be overcome. As run-of-mine lignite typically contains 30 to 50 percent bed moisture, transportation is prohibitive for other than short-haul destinations. One way around the problem is lignite dewatering. Another method is the conversion of lignite into a more easily and economically transportable fuel via gasification. Once gasified, the produced gas may be burned as a low energy fuel, or converted to a liquid fuel such as methanol. In both cases, the fuel value and, thus, the utility of lignite are being greatly increased.

Gasification Technology

There are three types of coal gasifiers currently in commercial use or development: fixed-bed, fluidized-bed and entrained-bed. The properties of each type of gasifier determine its suitability for any particular situation. Table 2 compares typical parameters of these gasifiers and acts as a first guide in their selection and design.

Thermal efficiency is the same for all types of gasifiers; however, the fixed-bed gasifier produces tar/oil which, when included in the energy balance, increases the efficiency. While fixed-bed gasifiers allow greater turndown capacity (the fraction of rated output at which the gasifier is still able to operate) they require greater response time to regain rated gas output.

TABLE 2. TYPICAL PARAMETERS OF COAL GASIFIERS
(Adapted from Baker, et al., 1979)

	Fixed-Bed (Single Stage)	Fluidized-Bed	Entrained-Bed
Coal Feed Size	13-38 mm	10-100 mesh	70% 200 mesh
Permissible Coal Types	Slightly Caking All (with agitation)	Slightly Caking	All
Capacity, tonnes/day	2.4-90	650-900	600-800
Carbon Conversion, %	80	50-80	90
Residence Time	1-3h	20-40 min.	1S
Thermal Efficiency, %	70-80	70	70
Exit Gas Temp., °C	370-600	700-875	1100-1500
Constituents Carried in Gas Product	Coal Dust Tar/Oil	Coal Dust Ash	Coal Dust Ash
Turndown Capacity, %	10-20	30-40	30-60
Availability, %	95+	90	90

The three types of gasifiers differ mechanically in coal particle velocity. The fixed-bed gasifier comprises, in reality, a column of coal which slowly moves downward under the influence of gravity. Ash is removed from the bottom, and gasifying agents, oxygen or air, and steam are fed upward from the bottom. In a fluidized-bed gasifier, coal particles are suspended by the reactant gas, and move in random motion like a boiling liquid. In an entrained-bed gasifier, the high velocity of the reactant gas combined with the small coal particle size, cause the gas to entrain and carry the particles. Reaction is instantaneous.

The following criteria will determine the suitability of a particular gasifier type with respect to the set of requirements and constraints present:

1) required rate of energy production and physical size constraints;
2) maximum turndown capacity requirements and response time;
3) product gas requirements (heating value, purity and cleanliness);
4) pressure and temperature constraints;
5) coal availability, type and cost; and
6) producer/consumer location and interactions.

Since a fixed-bed, single-stage gasifier was used in the experimentation of Phases I-IV, the chemistry and mechanics of this gasifier are discussed in greater detail below.

The fixed-bed gasifier exhibits excellent thermal and carbon conversion efficiencies due to the countercurrent movement of coal and gas feeds (exit streams pre-heat incoming streams) and the extended residence times. However, the long residence times and the limitation on the vessel diameter resulting from the required even distribution of feed coal, ash and gas, limit the capacity of the fixed-bed unit to about 10 percent of the other gasifier types.

Figure 2 is a schematic cross-section of a fixed-bed gasifier showing the various temperature zones encountered and chemical reactions occurring. Referring to Figure 2, an explanation of what occurs in each zone follows:

Drying Zone: Raw coal feed and hot product gases come into contact, resulting in drying of the coal.

Devolatilization Zone: Volatile matter including methane and carbon dioxide are driven off. As temperature increases, organic sulphur is driven off as H_2S and nitrogen and ammonia are released. Oil and tar are distilled from the coal, leaving char.

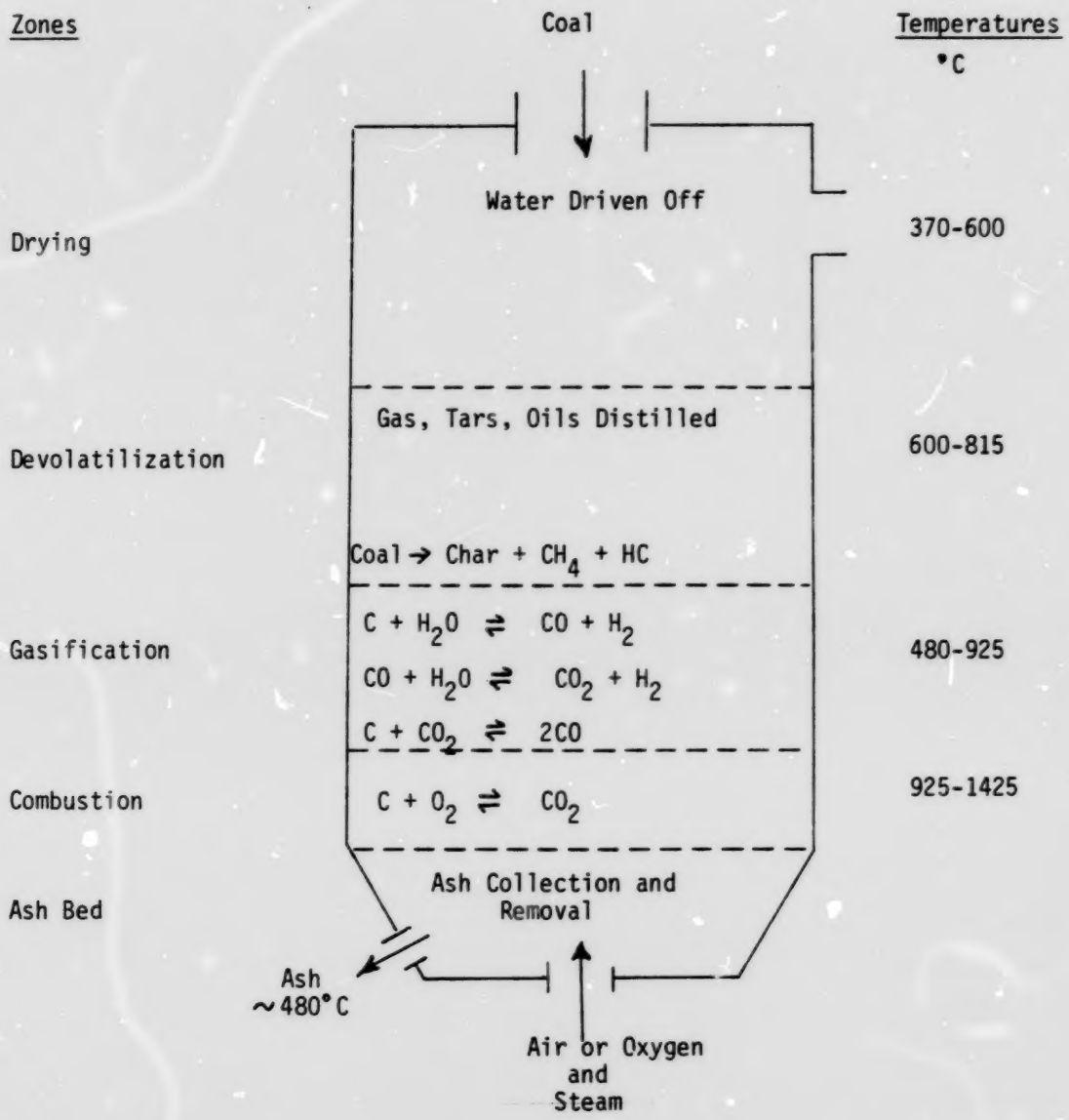

Figure 2. SCHEMATIC OF FIXED-BED GASIFIER (Adapted from Baker, et al., 1979)

Gasification Zone: Char, steam and combustion gases come into contact. Hydrogen is produced along with either carbon monoxide at high temperature or carbon dioxide at lower temperature, from endothermic reactions.

Combustion Zone: Char (carbon) reacts with oxygen to form carbon dioxide. Supported by layer of ash.

Ash Bed: Distributes and pre-heats incoming reactant gas stream.

Coal Char Gasification Kinetics

There exists an obvious advantage in studying coal char kinetics rather than whole coal reaction kinetics. It is relatively easy to conduct experiments under conditions of differential gas conversion, whereby the composition of the gas in contact with the coal char is known and remains constant. This facilitates the analysis of experimental kinetic results. This procedure is usually applied to the fixed-bed flowing gas systems as used throughout this work. When studying coal gasification, the kinetic data obtained after the initial devolatilization, are representative of those obtained from coal char-only gasification. Not only do the results depend on different coal types, but also on differences in the procedures employed in preparing the chars from these coals. For instance, if the charring temperature is low and the residence time sufficiently short, the resultant coal char can exhibit initial rapid-rate methane formation.

Johnson (1974) showed that pretreatment can affect the reactivity of coal chars. Even in those cases where these chars have been subjected to sufficiently severe pretreatment conditions, negligible rapid-rate methane activity remained.

The following coal char gasification reactions have received most attention in recent years. This has been a direct result of renewed interest in developing energy gases:

$$C + 2H_2 \rightleftharpoons CH_4 \quad (1)$$

$$C + CO_2 \rightleftharpoons 2CO \quad (2)$$

$$C + H_2O \rightleftharpoons CO + H_2 \quad (3)$$

Because of the favourable effect of pressure on the carbon/hydrogen reaction, this reaction has been studied almost exclusively at elevated pressures. The carbon/hydrogen reaction is particularly important for the production of high-energy gas. Reactions (2) and (3) are of importance during the production of low-and-high energy gases. Reactions (1) and (2) can take place in a stand-alone fashion in gasification systems roughly as dictated by their stoichiometry. The steam/carbon reaction (3), on the other hand, cannot generally occur alone under conditions of integral gas conversions. Because of the water/gas shift reaction (4):

$$H_2O + CO \quad CO_2 + H_2, \qquad (4)$$

carbon dioxide can be formed even with a pure steam feed gas and can react in competition with the steam/carbon reaction according to reaction (2) at high or low pressures. If pressures are sufficiently high, methane can be formed according to reaction (1) from hydrogen produced from both the steam/carbon reaction as well as the water/gas shift reaction.

It should be realized that the reactions shown here describe only overall stoichiometry in limiting cases. The reactions do not imply fundamental reaction steps. Therefore, in experiments involving complex gasification systems containing steam, hydrogen and carbon oxodes, only overall stoichiometry has been determined. To aid kinetic formulation, individual reactions have been postulated; however, such reaction schemes tend to be more arbitrary than those that could be obtained from more sophisticated techniques, e.g. isotope tracers. Gasification reactions are usually studied under isothermal conditions, and in most experiments the carbon gasification rate, R, has been defined by the expression

$$R = \frac{dX/dt}{1-X} \qquad (5)$$

where X = fraction of initial carbon converted
t = time.

R is sometimes referred to as the "Specific" carbon gasification rate. The above expression implies that if the absolute carbon gasification rate (moles of carbon gasified per unit time) under constant environmental conditions is proportional to the amount of carbon present at any time, R will remain constant with increasing conversion, X. This has indeed been found to be the case for carbon conversion fractions up to 80%. In a number of cases, however, some transient behaviour has been observed at levels of carbon conversion less than about 10%. At carbon conversions above 80% the limited experimental data suggest that the specific gasification rates may decrease somewhat (Van Der Heijden, et al., 1983). It appears, therefore, that the approximation of relatively constant specific gasification rates is applicable over a broad range of carbon conversion. However, this is at best applicable only to the gasification of chars in the absence of significant catalytic effects from natural or added impurities. The activity of catalyst present in the char can vary substantially during the course of gasification, and lead to significant variations in the specific gasification rates.

The anomalous behavior at low carbon conversion levels can be explained as resulting from possible changes in the pore structure of coal particles which can occur during devolatilization. This leads to the possible inhibition of gaseous diffusion during subsequent gasification. Initial specific rates may be slow when this inhibition occurs, but may increase with increasing conversion as restrictions are removed and more of the internal

surface is exposed to the reacting atmosphere. The general assumptions made in modelling heterogeneous reactions between solid particles and gases are:

a) char particles can be considered to be carbon spheres in an essentially infinite gas stream;
b) the gas phase reactant first diffuses to the solid surface or into the pores in the char, and then absorbs on and reacts with the surface; and
c) the gas phase products desorb and diffuse away from the char particle.

The rate limiting step in this model can be chemical (adsorption of reactant, reaction, desorption of products) or diffusional (bulk phase or pore diffusion of reactants or products).

Walker, et al. (1959) and Gray, et al. (1974), among several other investigators, have postulated the existence of different temperature regimes in determining which model is controlling. At low temperatures, chemical reaction kinetics is the rate determining step, while at increased temperatures, control is characterized by both chemical reaction and pore diffusion. At very high temperatures the limiting factor is bulk mass transfer.

In general, rates of carbon oxidation by steam and carbon dioxide are much slower than the reaction of carbon with oxygen. The hydrogen/char reaction is several orders of magnitude slower than the steam/char and carbon dioxide/char reactions.

In the detailed discussions on the work conducted the focus will be primarily on the behaviour of coal chars, although pertinent results obtained with other carbon solids will be considered.

Methods of Predicting Reactivity Parameters for Gasification of Lignites

Performing bench scale gasification studies to obtain system scale-up parameters requires a large number of experiments, in order to evaluate the effect of critical process variables on the overall system performance. During the evaluation of the data collected throughout Phases I-IV of this program, certain methods of data analysis and extrapolation were tested. These techniques, if considered in the initial design of an experimental schedule, could reduce the number of experiments necessary to obtain critical data, while reducing the extent of numerical analysis required.

I. Predicting Reactivity from Coal Composition

In the catalytic studies performed on Saskatchewan lignite it was demonstrated that predictions of lignite gasification reactivity could be made solely on the basis of lignite alkali metal concentration. Actual lignite char gasification carbon conversion was predictable to within 20% for ROM coals, on the basis of Na^{+} and Ca^{++} ions only.

II. Reactivity Prediction Based on Half-Time Determinations

The two kinetic models used to evaluate lignite carbon conversion data can be expressed in terms of a half-time, $t_{1/2}$. The half-time is simply the time necessary to convert half the initial carbon in the char into carbon oxides. The integrated kinetic relations when expressed on this basis are:

$$k_1 = \frac{\ln(2)}{t_{1/2}} \tag{6}$$

for first order kinetics; and,

$$k_0 = \frac{0.5}{t_{1/2}} \tag{7}$$

for zero order kinetics,

where k_1 and k_0 are the first-and zero-order rate constants, respectively. Thus, by determination of the parameter $t_{1/2}$, it is possible to evaluate the carbon conversion characteristics of the coal at the operating conditions used for the experiment. This method is convenient in that the analysis requires only one

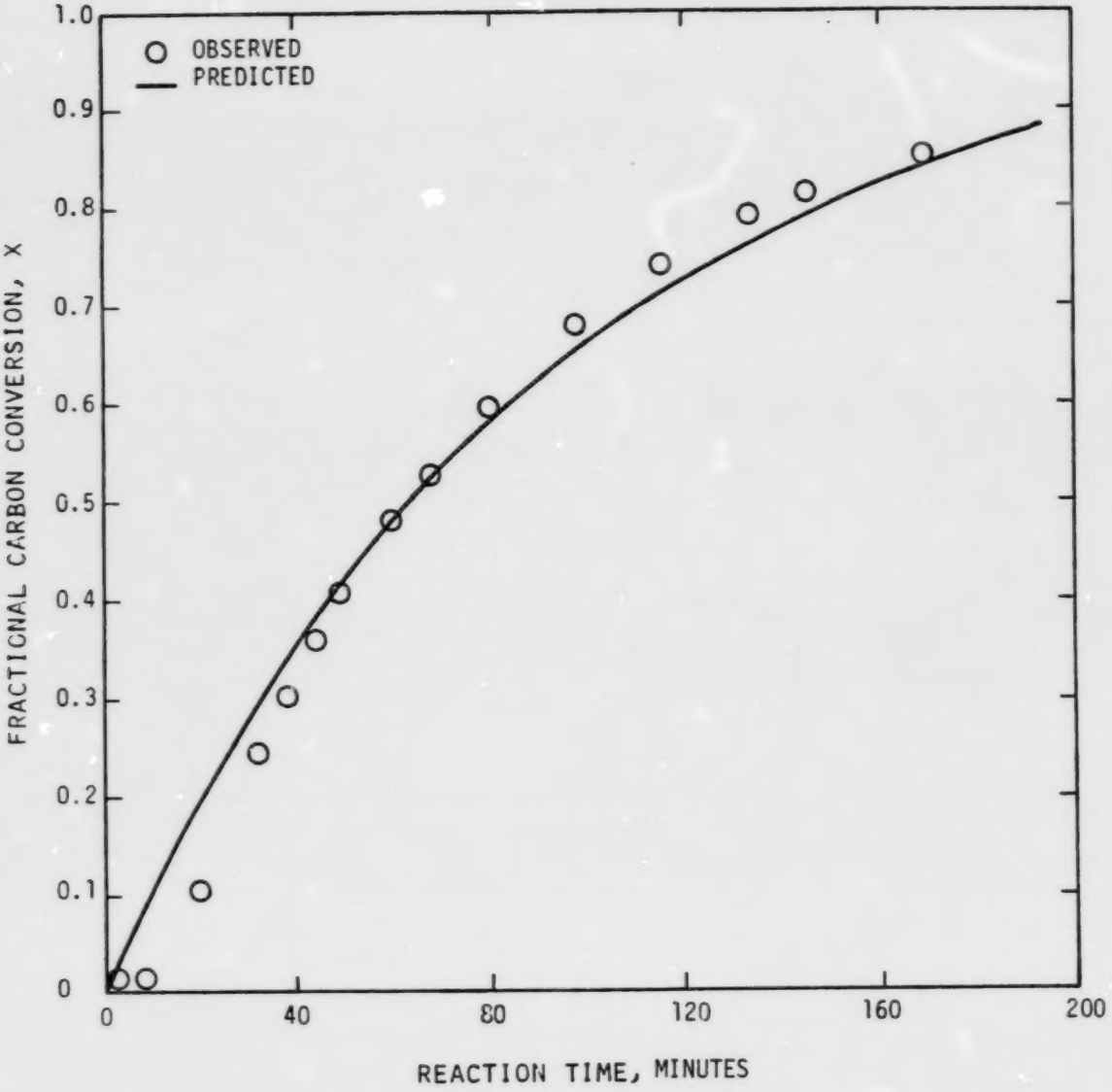

Figure 3. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF LIGNITE CHAR (PREDICTION) BASED ON k_1 CALCULATED FROM $t_{1/2}$)

experimental data point, once the order of reaction is known.

The method was found to be very accurate when used for char gasification kinetic evaluations. A sample plot of experimental and predicted fractional carbon conversion data for the steam gasification of lignite char is shown in Figure 3. Even when the method is applied to coal gasification where the volatile matter is evolved during the first twenty or so minutes of reaction time the method provides a very good approximation of lignite gasification behaviour as shown in Figure 4. Thus, once the reaction order is known, further experimentation would be required only for the determination of the half-time to define the coal gasification reactivity at a different set of conditions.

III. Reactivity Prediction on the Basis of Individual Reactions

Observation of steam/air gasification data from the various phases indicated that the carbon/steam reaction may behave independently of other gasification reactions. In order that this theory holds true the oxygen consuming reaction (8):

$$C + O_2 \longrightarrow CO_2 \qquad (8)$$

must proceed considerably faster than the steam consuming reaction (3):

$$C + H_2O \rightleftharpoons CO + H_2. \qquad (3)$$

Otherwise steam/air gasification would not proceed according to zero order kinetics but rather at some fractional order between

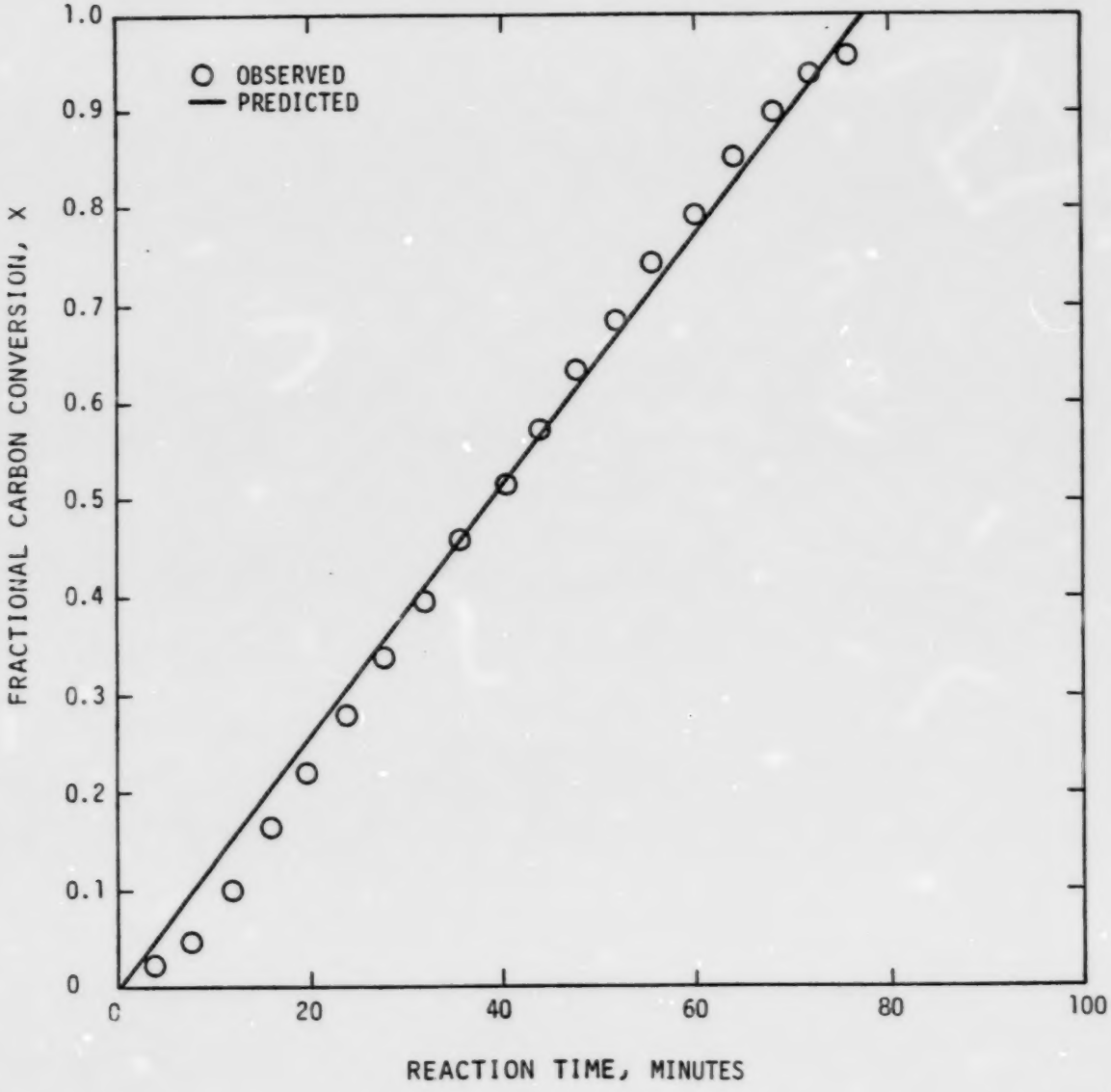

Figure 4. COMPARISON OF PREDICTED AND OBSERVED CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF ROM LIGNITE CHAR (PREDICTION BASED ON k_o CALCULATED FROM $t_{\frac{1}{2}}$)

zero and one.

It is known that at the reactor temperatures used throughout this work reaction (8) will consume incoming oxygen almost instantaneously and for typical gasifier operation the rate of carbon conversion due to oxygen will be dependent only on the flowrate of air into the gasifier. The consumption of carbon due to steam depends on the kinetics of the reaction at the temperatures and pressures under consideration and can be evaluated from the experimental half-time for steam-only char gasification at identical operating conditions. The results presented graphically in Figure 5 show that the assumption is indeed correct and the oxygen consuming reaction proceeds at about four times the rate of reaction (3). The fractional carbon conversion due to reactions (8) and (3) combined is compared with actual carbon conversion data in Figure 6. The extent of carbon conversion due to reactions (8) and (3) underestimates actual data by 24%.

The previous analysis, however, omitted the Boudard reaction (2):

$$C + CO_2 \rightleftharpoons 2CO \qquad (2)$$

which may account for this discrepancy. The double arrows in reaction (2) signify that the extent of carbon conversion should be dependent on equilibrium conditions inside the reactor.

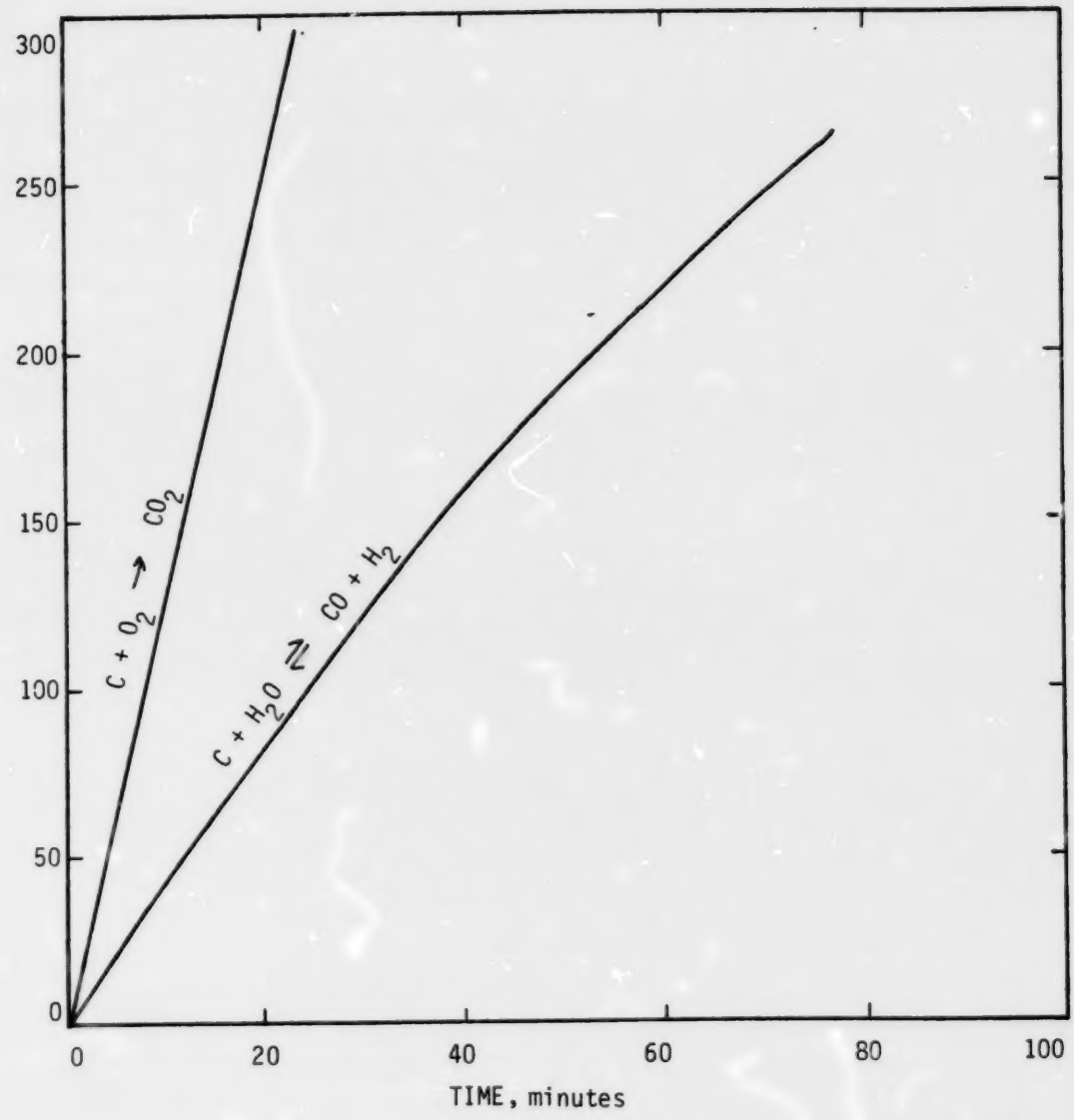

Figure 5. CUMULATIVE CARBON CONVERSION DUE TO STEAM AND OXYGEN

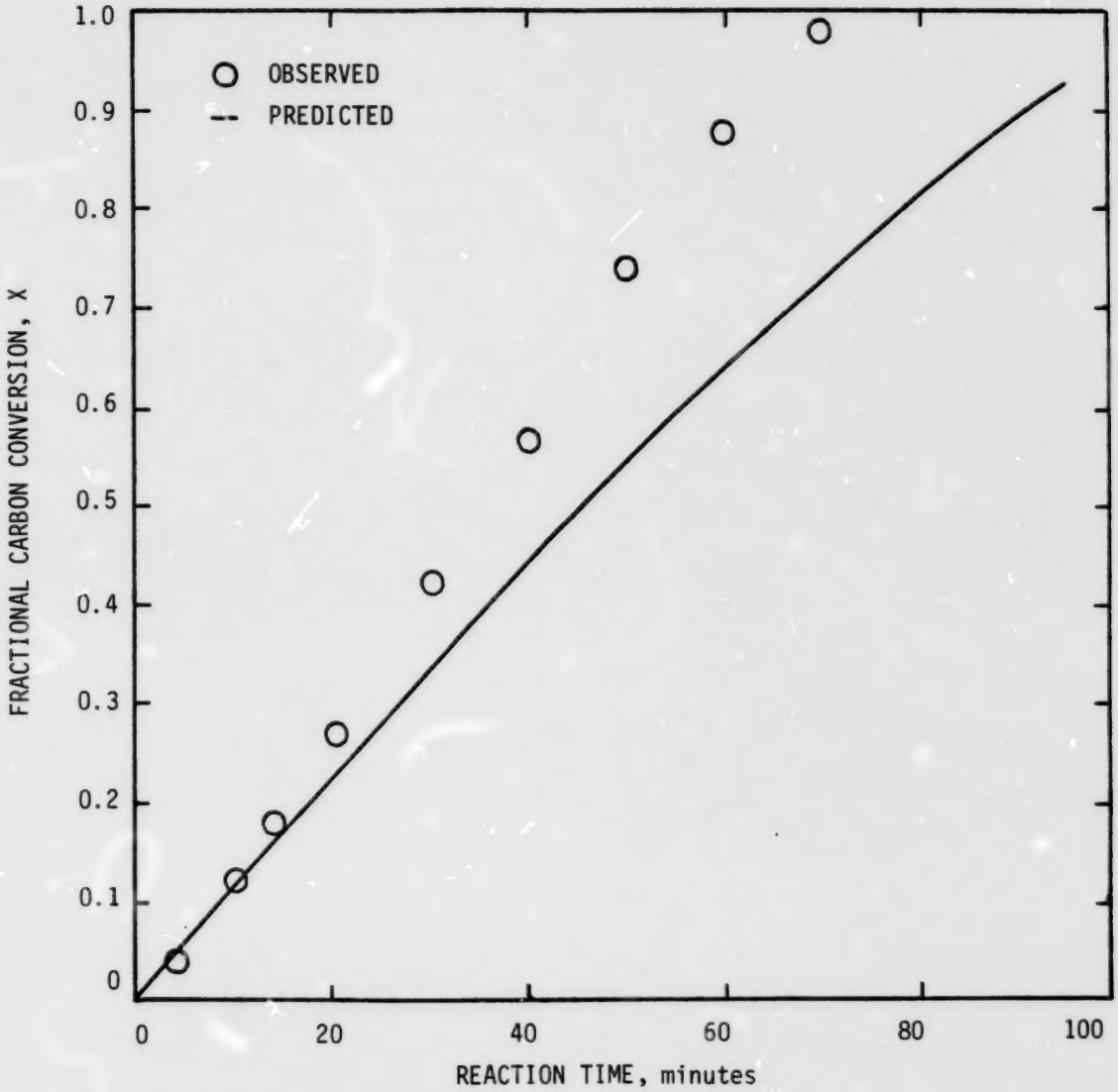

Figure 6. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF LIGNITE CHAR (PREDICTION BASED ON THEORETICAL TREATMENT OF REACTIONS (3) AND (8))

Assuming that the amount of CO_2 available in the reactor exit is at equilibrium with CO, a series of simultaneous equations can be solved to determine the amount of carbon removed by reaction (2').

Figure 7 shows the very good correlation between actual carbon conversion data and that predicted by the theoretical analysis of reactions (2), (3), and (8).

The results of this theoretical analysis demonstrate a way in which extrapolative methods can reduce the number of required experiments. From one convenient measurement of $t_{1/2}$ for steam gasification, the result can be extrapolated to accurately predict steam/air char gasification behaviour. Care must be exercised, when utilizing this analytical method, to make sure that the gasifier conditions are such that the overall rate is primarily chemical reaction-controlled. If the gasification is occurring in a diffusion-controlled regime, the results of extrapolation from steam-only to steam/air coal gasification will be erroneous.

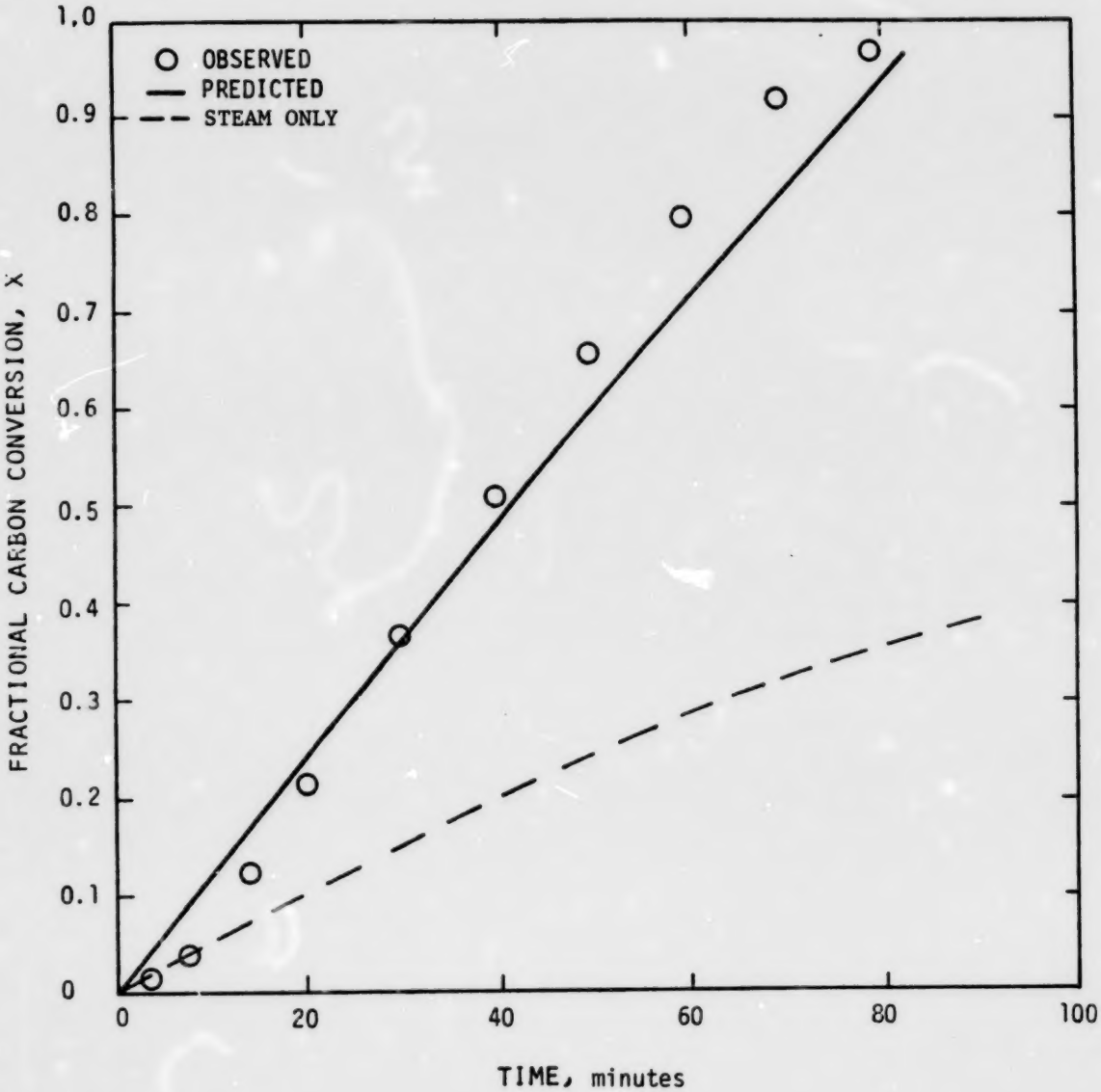

Figure 7. COMPARISON OF PREDICTED AND OBSERVED ROM CARBON CONVERSION FOR THE STEAM/AIR GASIFICATION OF LIGNITE CHAR (PREDICTION BASED ON THE THEORETICAL TREATMENT OF REACTIONS (2), (3) AND (8))

SUMMARY OF EQUIPMENT SETUP AND EXPERIMENTAL PROCEDURE

Over the course of the past four Phases of the Lignite Reactivity program, the design of the gasification reactor feed and effluent trains has evolved as experience with the equipment was accumulated. The experimental procedure has also been modified as different types of data were required. The following description outlines the general experimental setup and procedure, and details the developments that have occurred.

Equipment Setup

The reactor, a fixed-bed gasifier, consists of a 102 mm O.D. X 51 mm I.D. Hastelloy C-276 cylinder with an overall length of 1.53 m. The top one-fifth of the reactor (305mm) has a reduced I.D. of 32 mm. Both end closure assemblies are fabricated from 304SS stock.

Heat is supplied to the gasifier via a three-zone, 6kW electric furnace (Lindberg, model 54557). Temperature measurement is accomplished with a type K (chromel/alumel) thermocouple mounted in a stainless steel thermowell in the bottom closure. The thermowell protrudes through a perforated carbon steel disc (used to support the coal in the gasifier during gasification), about 60 mm into the coal bed. The reactor is shown in cross-section in Figure 8.

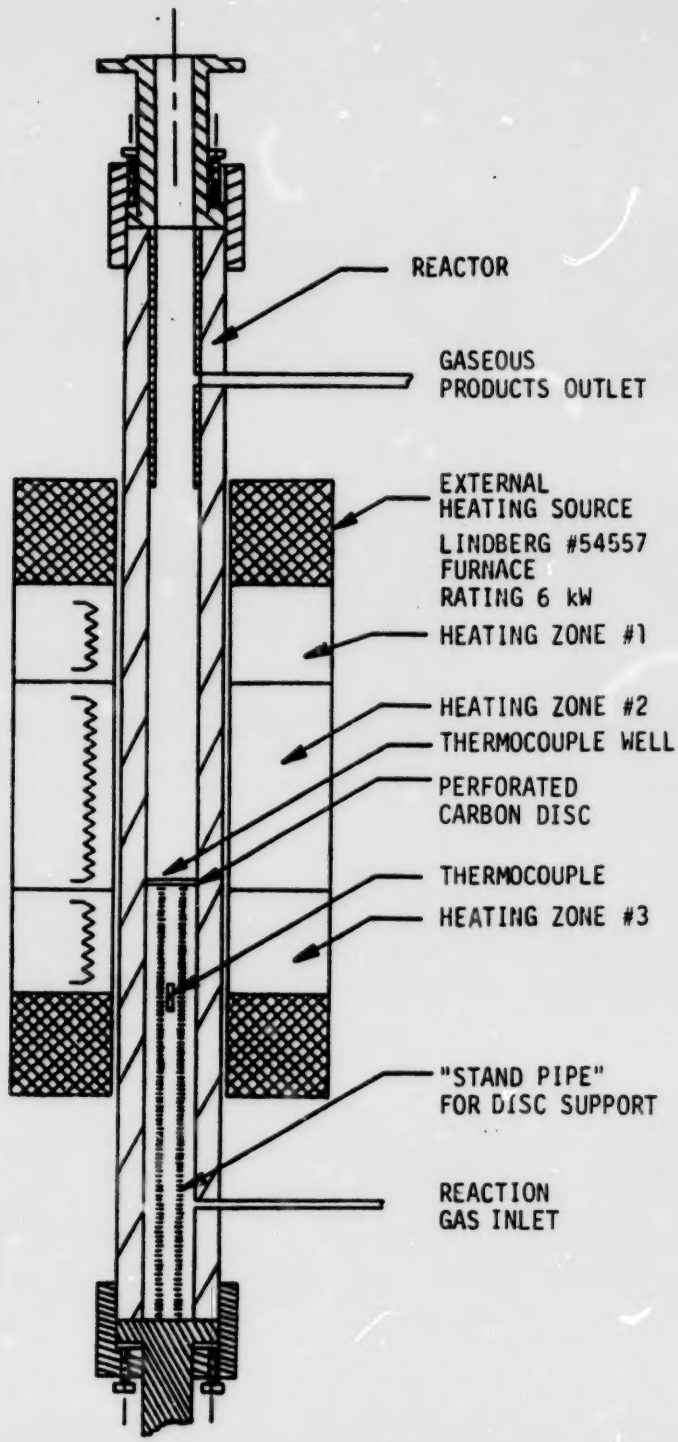

Figure 8. REACTOR CROSS—SECTION

A low-pressure reactor (150 kPa max.), fabricated from Schedule 160 seamless carbon steel tubing, was used for some early experiments. As the reactor was limited in scope, it was replaced by the high-pressure reactor of Figure 8, and, for continuity, experiments performed in the earlier reactor were repeated in the new high-pressure (6 MPa max.) setup.

Coal is fed to the pre-heated reactor *via* a tubular, pressurized coal hopper, joined to the top of the reactor by a ball valve. Originally, batch operation was accomplished with a full-bore valve. Later the valve was modified for semi-continuous, discrete operation. A modified, 25 mm WK-Dynaseal ball valve was equipped with a star insert, dividing the bore into two compartments, capable of delivering 16g of coal with each 180-degree rotation. Pressure inside the hopper was maintained at reactor pressure to minimize gas leakage through the ball valve.

Compressed air was supplied from a standard gas cylinder, with the flowrate being determined by a calibrated metering valve. Water was fed *via* a high pressure metering pump from a weighed water reservoir to a boiler. Steam and air were mixed prior to being fed to the bottom of the reactor.

While the coal feeding arrangement had evolved into a semi-continuous mechanism, ash removal from this non-slagging gasifier was handled batchwise, with disassembly and cleaning required after each day's run.

The remainder of the reaction product processing train went through several modifications. Basically, however, gases were removed from the reactor continuously and passed through a knock-out pot and/or condenser, where liquid products and tars, formed during gasification, were collected. After quenching, any particulate that still remained with the gases was removed by filtration. The gases were next depressurized via a back pressure regulator, saturated, and then measured volumetrically in a wet test meter. Provision was made for periodic sampling and gas chromatographic analysis, or direct analysis using Riken, model RI-550A, non-dispersive, infrared gas analyzers (CO, CO_2 and CH_4 were monitored). Figures 9, 10, and 11 indicate the original experimental set-up, the first modification and the second modification, respectively.

In Phase IV, the hopper was completely removed and the coal charge added batchwise. Devolatilization gases were collected through the top of the reactor, bypassing the gas cleaning train. Condensate collection was superfluous in this set of experiments, and was discontinued. Low CH_4 values and the eventual malfunctioning of the CH_4 infrared gas analyzer allowed only CO and CO_2 monitoring.

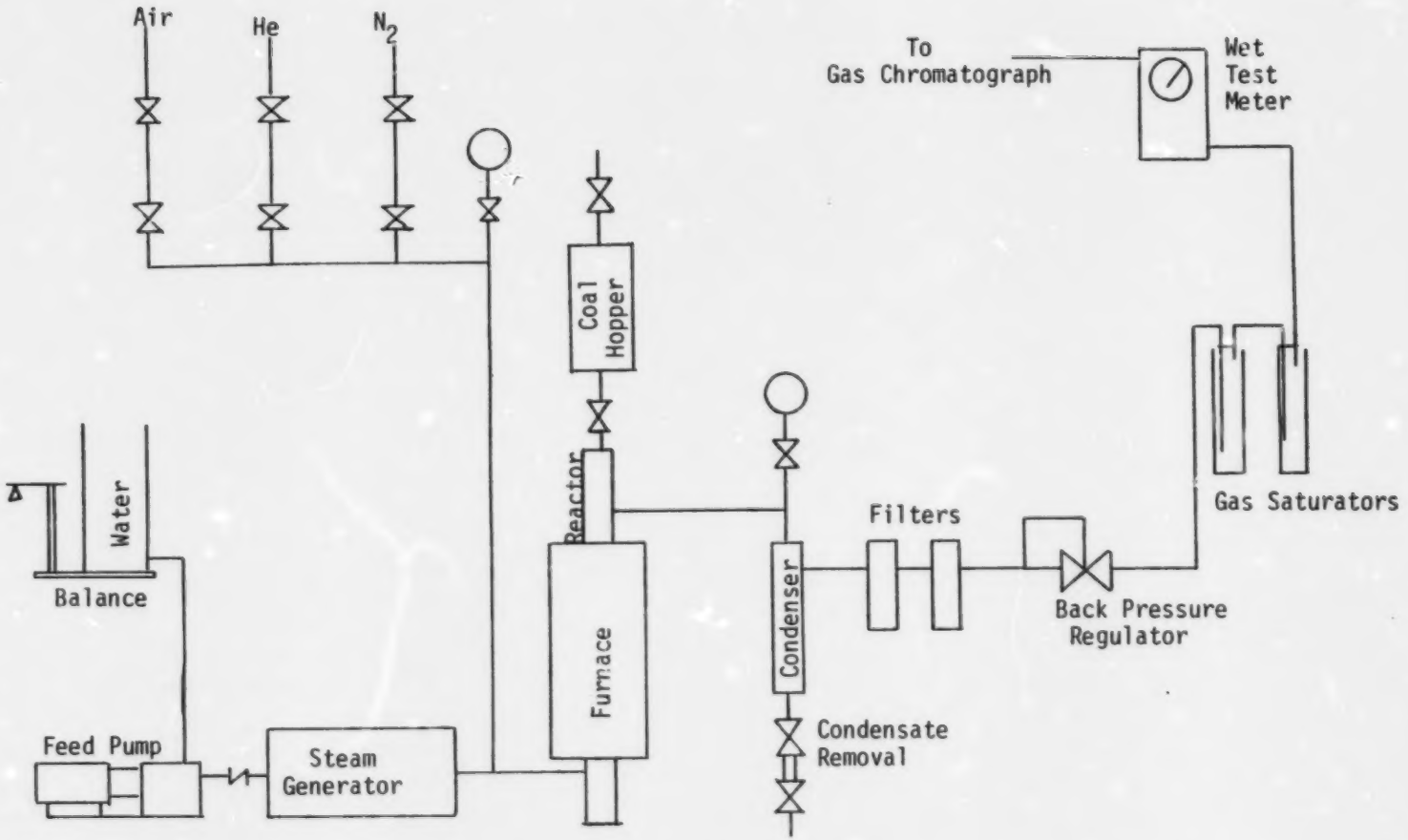

Figure 9. ORIGINAL EXPERIMENTAL SETUP

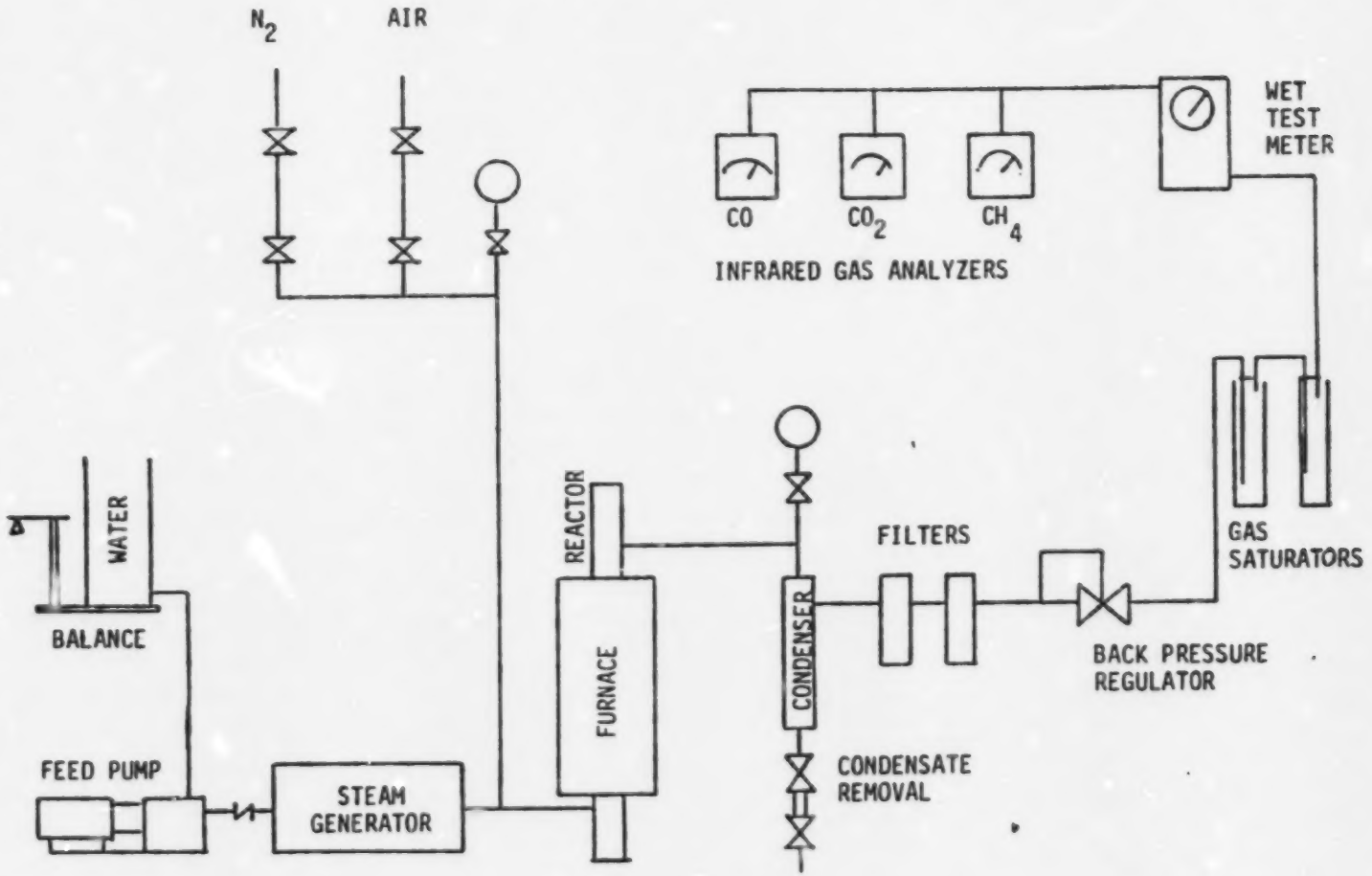

Figure 10. EXPERIMENTAL SETUP MODIFICATION FOR CATALYTIC STUDIES

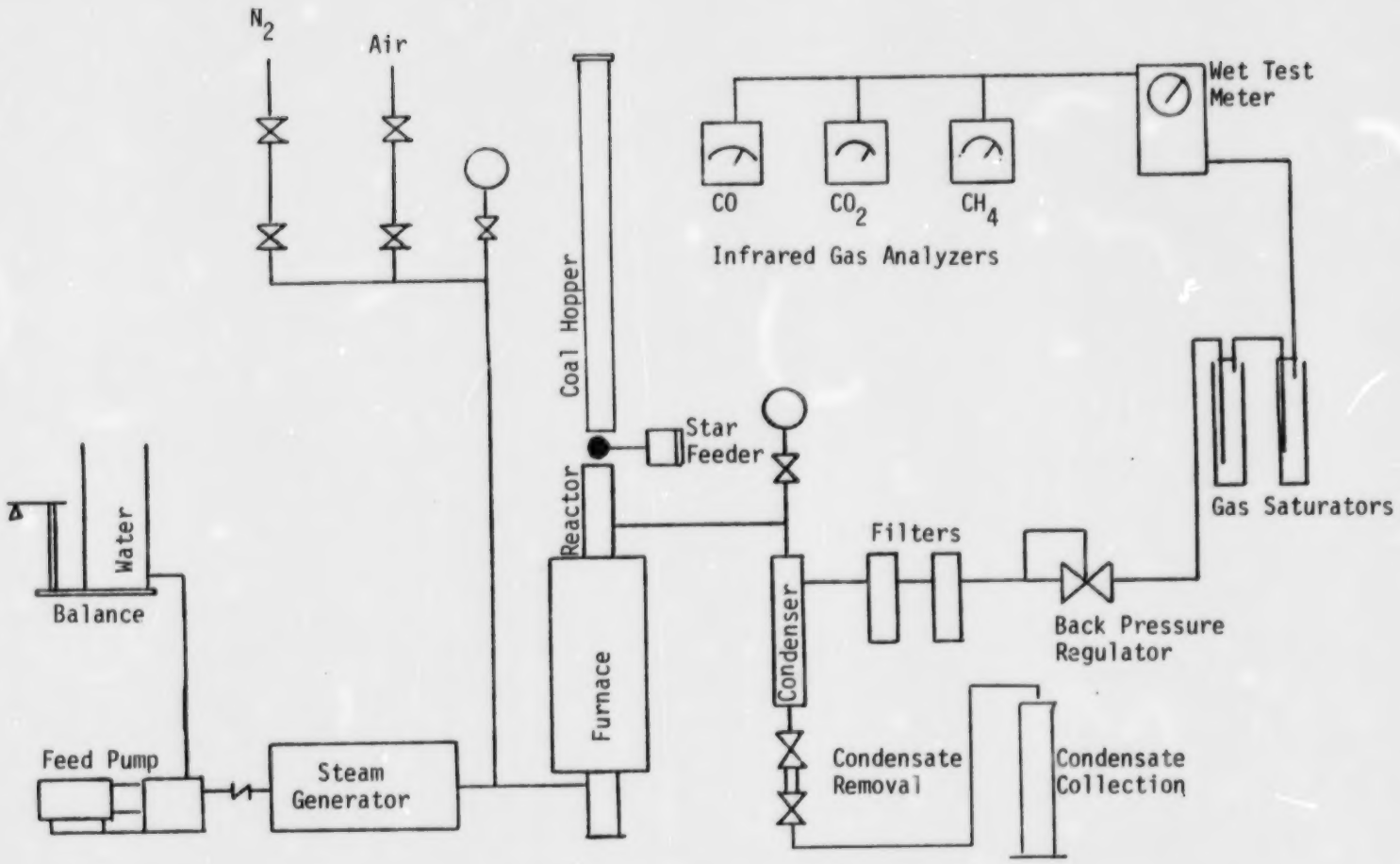

Figure 11. EXPERIMENTAL SETUP MODIFICATION FOR EXTENDED OPERATION

Experimental Procedure

In general, the gasification run procedure was similar through all four Phases of experimentation. However, the procedures followed in treating the product gases and effluent changed as the data required from the runs changed.

As a rule, the reactor was pressure tested cold with nitrogen or helium, and after depressurization, was preheated to the operating temperature. The boiler was also preheated at this time. When the desired temperature was reached, coal (Estevan or Coronach lignite) was placed in the hopper, and the gasifier was purged and then pressurized with helium. Coal was then introduced to the reactor by opening the ball valve (500g samples were introduced in the batch mode, and 400 g in 25 discrete doses in the semi-continuous mode followed by additional amounts at regular intervals). The steam and air flows were then begun, and the rest of the system was slowly opened up to the reaction atmosphere.

The end of the gasification reactions was indicated by either a drop in internal reactor temperature, a large increase in the oxygen concentration of the product gases, or the concentrations of both the CO and CO_2 in the off-gases dropping below one percent by volume. At this point, all flows were cut off and the reactor was allowed to cool overnight. (In early experiments cooling was

accomplished under a slow flow of nitrogen). Depressurization of the reactor was performed either before or after cooling. Once cool, the reactor was disassembled and the char/ash was removed. The knock-out pot was opened and samples collected.

Figure 12 shows a typical schedule of analyses performed on the feedstock, products and effluent stream (for Phase III experiments). Generally, analysis similar to this was carried out to a greater or lesser extent for all four Phases of experimentation, depending on the type of data required. For example, in Phase I additional petrographic analyses on the remaining char were carried out, and in Phase IV, condensate collection was omitted.

Sample preparation was required in Phase IV, in which the catalytic activity of calcium and sodium was examined. Blended, air-dried, ground and sieved coals were extracted with 2M HCl at 60°C to remove all calcium and sodium, and then water-washed at 60°C until all chloride was removed. Differing amounts of calcium and sodium were next added to the cation-free coals by ion exchange with calcium and sodium acetate solution, followed by water washing to remove excess acetate, and drying under nitrogen at 105°C. Other than this treatment, feedstock preparation for the other Phases consisted of the ordinary sizing and drying.

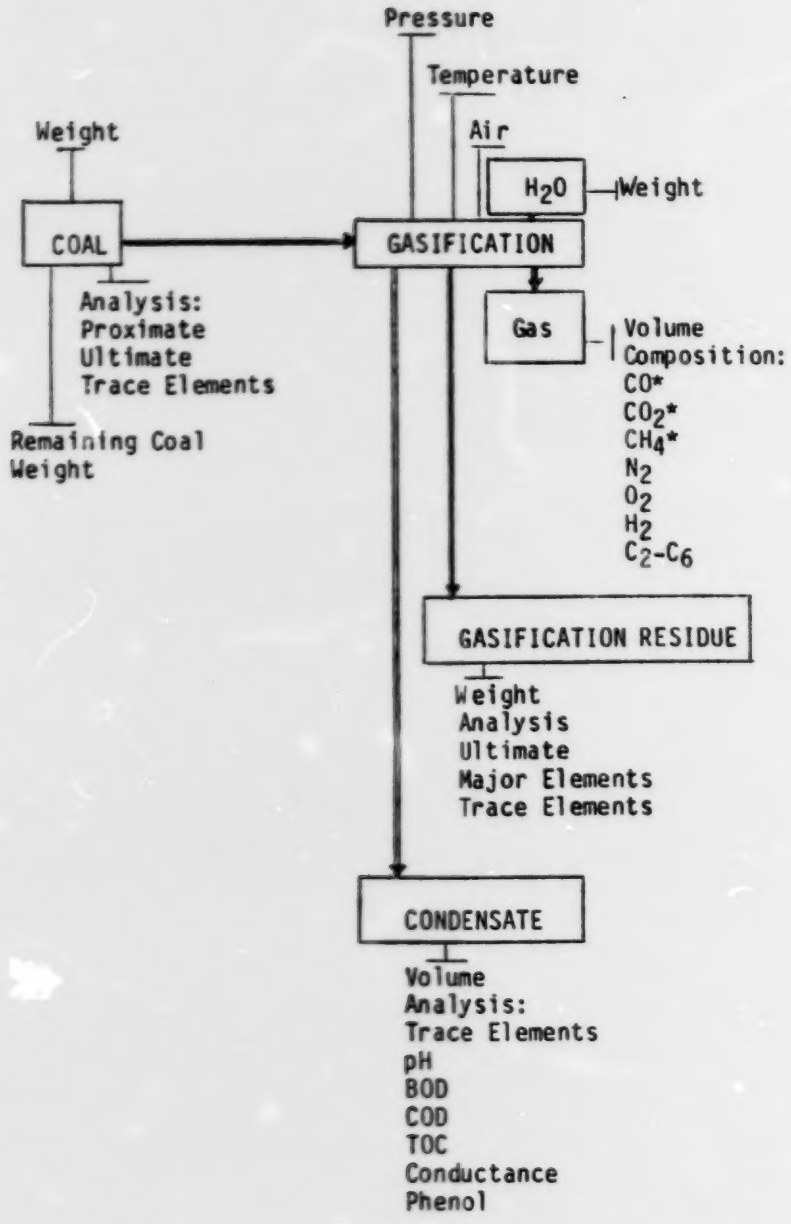

Figure 12. ANALYSES PERFORMED ON THE FEEDSTOCK AND EFFLUENTS FROM GASIFICATION RUNS IN PHASE III

DISCUSSION

Reaction Order for Air/Char Gasification

Carbon conversion data obtained from air gasification experiments were tested for fit to first and zero order kinetic models. The results presented in Table 3 and Figures 13 and 14, indicate an upward shift in the apparent reaction order as the flowrate of air fed to the gasifier is decreased. In order to explain this observation the work of other investigators was studied.

Most investigators correlate their data on the basis of first order oxygen concentration dependence. However, Smith and Tyler (1972) and Tyler, et al. (1976) indicate reaction orders which are close to zero, especially at high temperatures. Yet another possible explanation arises from the existence of diffusion limitations in the gasification of carbon. These depend on the chemical reactivity of the carbon as well as the pore structure characteristics. In situations where the chemical reactivity is low because of the inherent nature of the carbon or the reaction conditions employed, more severe diffusion resistance can be tolerated, without affecting the gasification kinetics, than would be the case with high chemical reactivity. Of course, high chemical reactivity is favoured by high temperatures. This can lead to the observation that there is a transition in the

TABLE 3. SPECIFIC REACTION RATES FOR AIR/CHAR GASIFICATION OF SASKATCHEWAN LIGNITES

Temperature (K)	Air Flow (Moles/Min)	Zero Order Fit k_o (Min^{-1})	First Order Fit k_1 (Min^{-1})	Conversion Range
1063	0.468	0.0073	0.0167	0.2 - 0.8
1003	0.468	0.0063	0.0143	0.2 - 0.8
1083	0.468	0.0078	0.0175	0.2 - 0.8
1023	0.468	0.0121	0.0345	0.3 - 0.9
963	0.371	0.0083	0.0181	0.2 - 0.8
973	0.371	0.0077	0.0172	0.2 - 0.8
1203	0.295	0.0079	0.0203	0.2 - 0.8

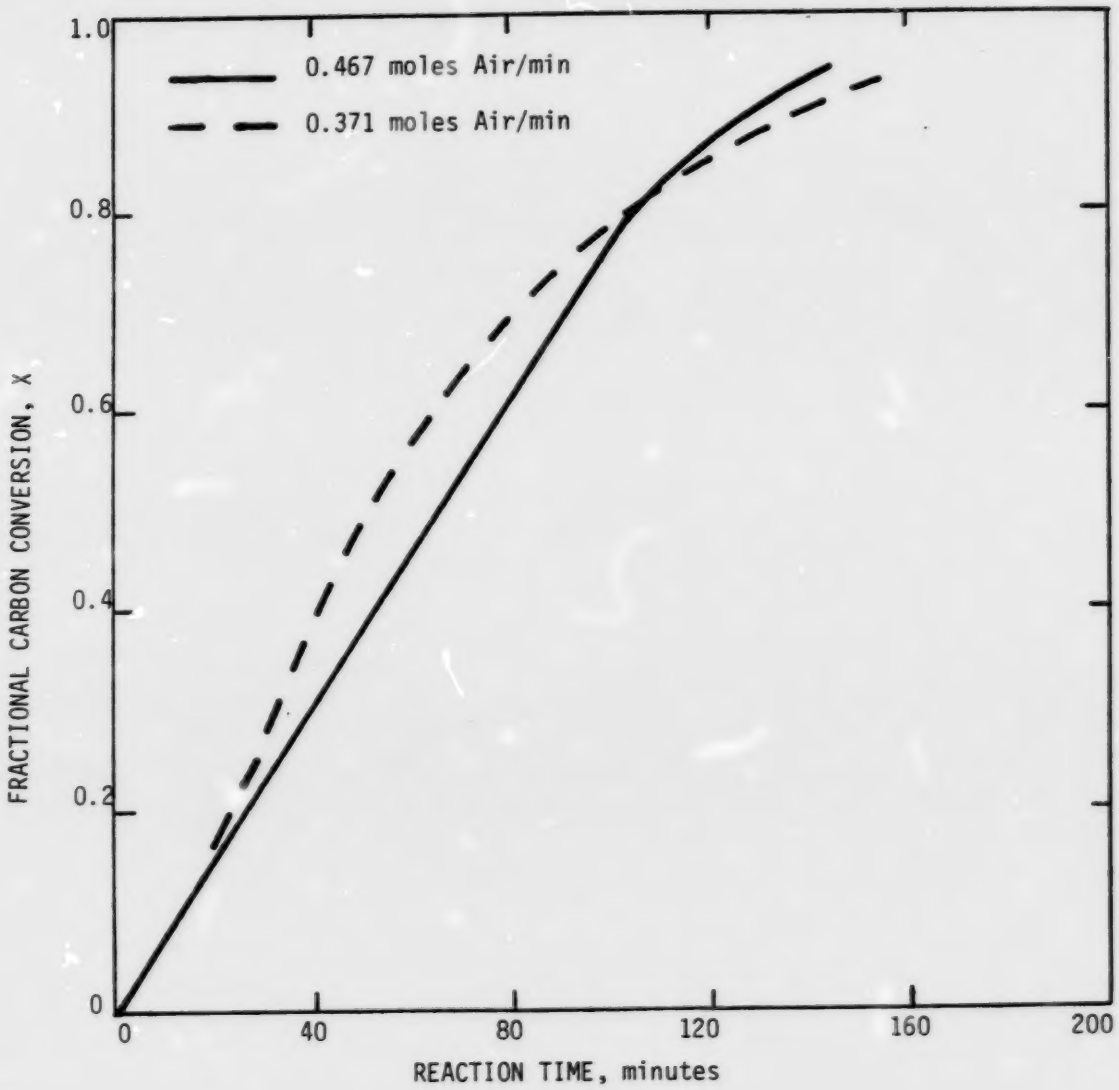

Figure 13. EFFECT OF AIR FLOWRATE ON REACTION ORDER n FOR AIR/CHAR GASIFICATION (ZERO ORDER)

TABLE 4. CARBON GASIFICATION RATES FOR AIR/CHAR GASIFICATION OF ESTEVAN LIGNITE AT 0.1 MPa

Temperature (K)	O_2 Fed (Moles/Min)	Experimental Rate (gC/Min)	Predicted Rate (gC/Min)
1063	.0980	1.22	2.258
1003	.0980	1.34	2.108
1083	.0980	2.00	2.276
1023	.0980	1.549	2.168
963	.0780	1.52	1.554
973	.0780	1.77	1.584
1203	.0620	1.44	1.476

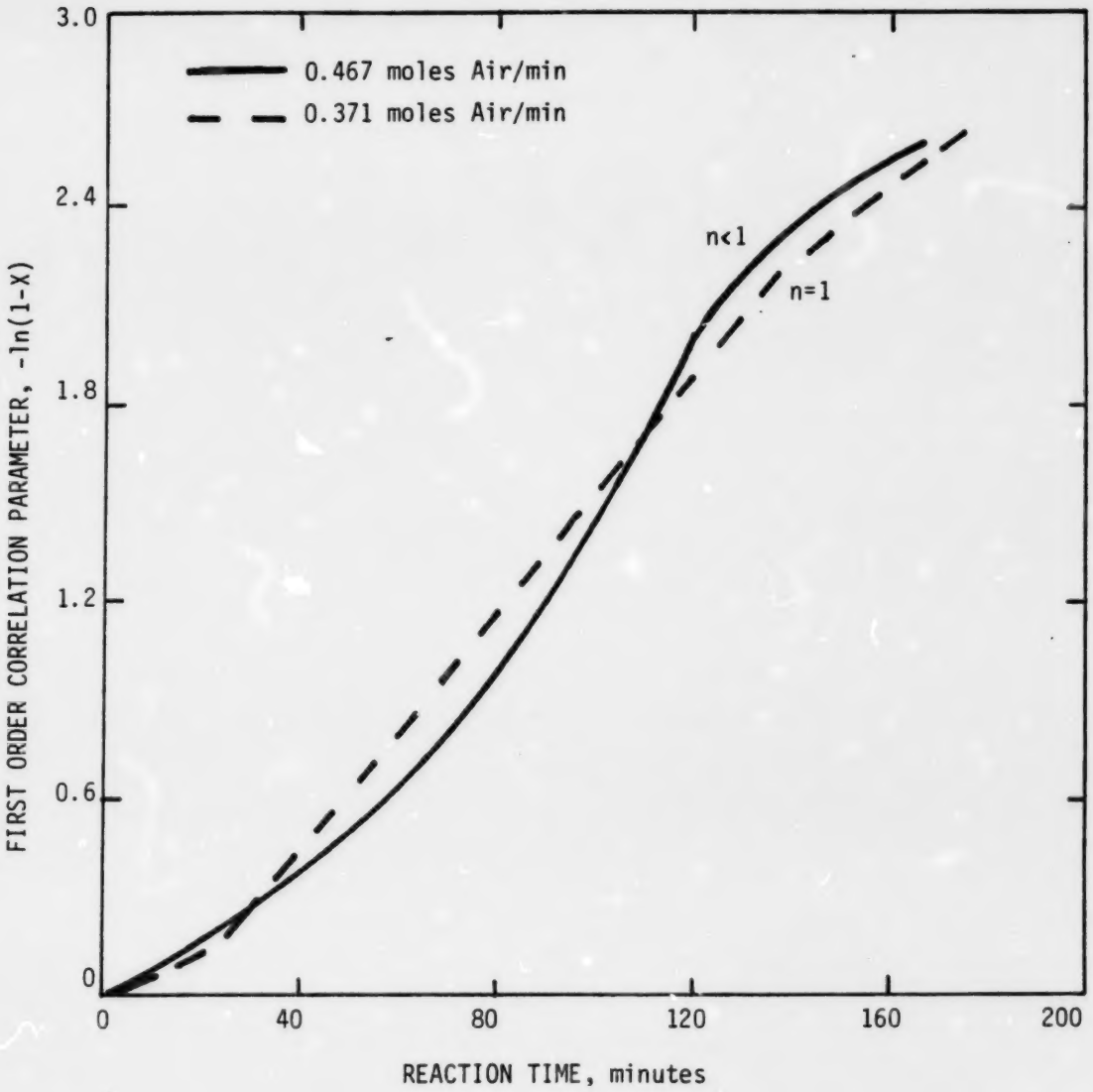

Figure 14. EFFECT OF AIRFLOWRATE ON REACTION ORDER n FOR AIR/CHAR GASIFICATION (FIRST ORDER).

controlling mechanism of solid/gas reaction from chemical control to diffusion control that occurs when the temperature increases. This transition is usually accompanied by a decrease in the overall temperature coefficient of the reaction.

Because of the complexity of pore diffusion processes during coal char gasification, quantitative predictions describing the interaction of chemical and diffusion phenomena would require, at the very least, a detailed characterization of variations in char pore structure. Although some information is available in the area much more is needed. No data is available on the coal chars used in this study.

Fortunately, however, for many of the conditions relevant to coal char gasification systems that have been studied, relatively little effect has been observed of particle size on reaction kinetics. In spite of this—even from an empirical standpoint—little basis exists to accurately predict under which conditions internal particle diffusion may become important in coal char gasification systems. This is due to the lack of systems in which the particle size of coal chars has been systematically varied.

Although very approximate considerations would suggest that chemical reaction control will predominate with most coal chars during gasification below 1000°C and particle sizes below approximately 2 mm, the possibility of diffusion inhibition should be considered at more severe conditions such as those likely to

exist in large steam/oxygen gasifiers. Even though such severe conditions are not likely reached in the experimental reactor used, the likelihood of this phenomenon cannot be ruled out.

Due to the wide variation in the reported findings of others it was felt that the best approach to evaluating this shift in reaction order would be to use a method that proved useful in previous phases. This approach involves analyzing on a theoretical basis the basic reactions occurring in air gasification processes. The reactions (8) and (2):

$$C + O_2 \longrightarrow CO_2 \qquad (8)$$

and

$$C + CO_2 \rightleftharpoons 2CO \qquad (2)$$

proceed independently and are controlled by the flowrate of air to the gasifier and equilibrium conditions inside the reactor respectively. Rates of carbon conversion based on this theoretical treatment are compared with experimental values in Table 4. Good agreement with the theoretical values would indicate that chemical reaction is controlling the rate of carbon gasification.

The results show that as the air flowrate is decreased the agreement between the two values becomes very good. At the highest air flowrate studied (.467 moles/min) the experimentally determined rates are substantially lower than the theoretical

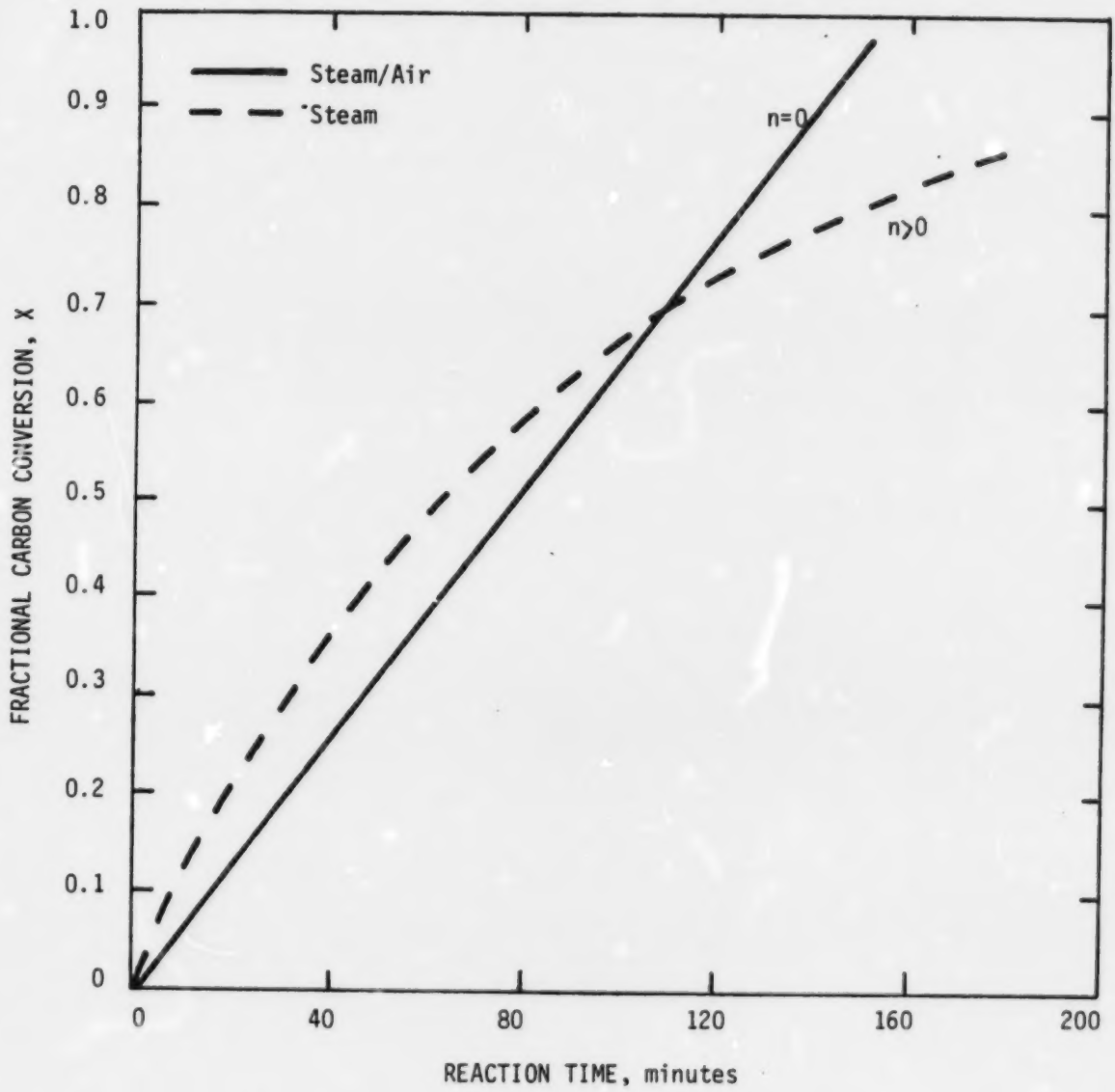

Figure 15. EFFECT OF REACTANT GAS TYPE ON REACTION ORDER n FOR CHAR GASIFICATION (ZERO ORDER)

values. Thus at very high rates of air flow some factor other than chemical reaction kinetics is controlling the observed rate of carbon conversion.

One explanation for these observations is that the air concentration on the active lignite sites is high enough that the Boudard reaction cannot proceed to any great extent due to N_2 poisoning, or that the higher linear velocities in the reactor system do not allow sufficient residence time for the slower Boudard reaction to take place. Whatever the reason for the observed shift, an examination of the Langmuir rate expression for the Boudard reaction confirms that this phenomenon would be observed.

The Langmuir rate expression for the Boudard reaction:

$$r_{co_2} = \frac{kP_{co_2}}{1 + aP_{co} + P_{co}} \qquad (9)$$

where k_1 a and b are functions of one or more of the rate constants characterizing the elementary reactions, P_{CO} and P_{CO} are the partial pressures of CO and CO_2, respectively, r_{CO} is the rate of carbon conversion due to CO_2, implies that, at high CO_2 partial pressures (ie. $bP_{CO2} >>$ equation (9) collapses to the form of a zero order expression in terms of CO_2 consumption which implies zero order with respect to the carbon in the char. On the other hand, when the Boudard reaction reaches the extent of its

equilibrium constraints, the rate of CO_2 consumption becomes dependent on the partial pressure of CO_2 in the reactor and first order kinetic behavior is approached.

The most important point to derive from this discussion is that, in air gasification processes, there is a definite limiting factor as to the quantity of air that should be fed to the gasifier per g carbon per unit time. In designing continuous flow, air blown, fixed gasifier systems, this is a factor which should require significant consideration in order that both the production of carbon monoxide and the rate of carbon conversion may be optimized. Unfortunately, the range in air flowrates used in these experiments does not allow quantitative recommendations as to the optimal rate to be used.

Catalytic Effect of Alkali Metal Cations on Lignite Char Reactivity

The relatively high gasification reactivity of lignite char compared to that of higher rank coals has been the subject of many investigations. Naturally occurring alkali metals such as calcium and sodium have been reported to contribute to the high gasification reactivity of lignite. These cations are essentially atomically dispersed throughout the lignite organic and inorganic

matrices.

Analyses of our experimental carbon conversion data indicated that steam gasification of lignite chars proceeded according to first order kinetics with respect to carbon conversion as indicated in Figure 15. On the other hand, steam/air char gasification data demonstrated zero order behaviour with respect to carbon conversion (see Figure 16). Therefore, in evaluating the effect of sodium or calcium concentration on char reactivity the following integrated rate expressions were utilized:

$$I(x) = x = k_o t \qquad (10)$$

for zero order kinetics

and

$$I(x) = -\ln(1-x) = k_1 t \qquad (11)$$

for first order kinetics.

A third (fractional order) expression, proposed by Nandi and Johnson (1979) and based on the shrinking core model for coal particle gasification, was also tested for fit to the experimental data. It was found, however, that a better fit was provided with either the first or zero order models presented here. Figure 17 presents a comparison of the fit between the first and fractional order models.

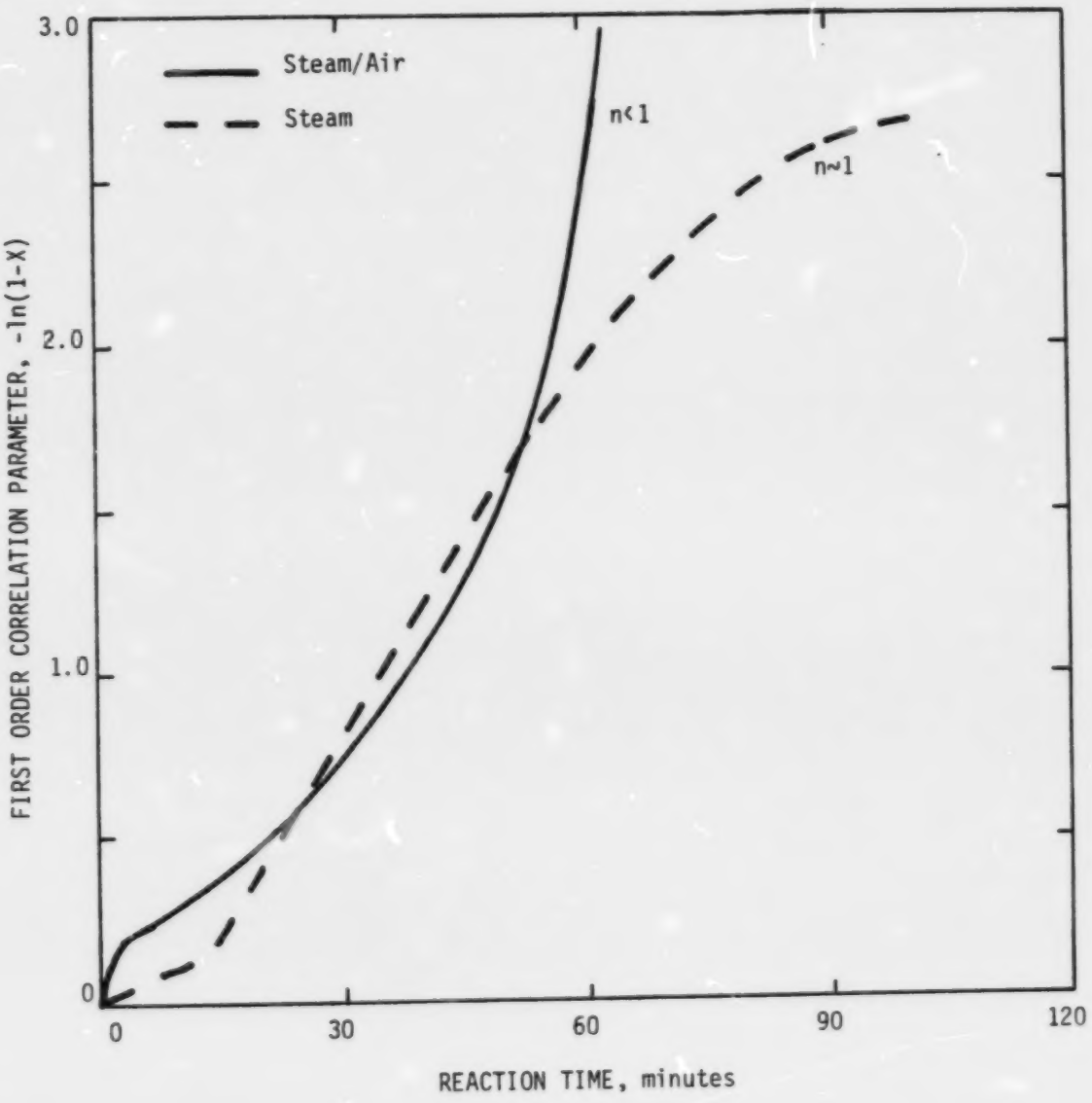

Figure 16. EFFECT OF REACTANT GAS TYPE ON REACTION ORDER n FOR CHAR GASIFICATION (FIRST ORDER)

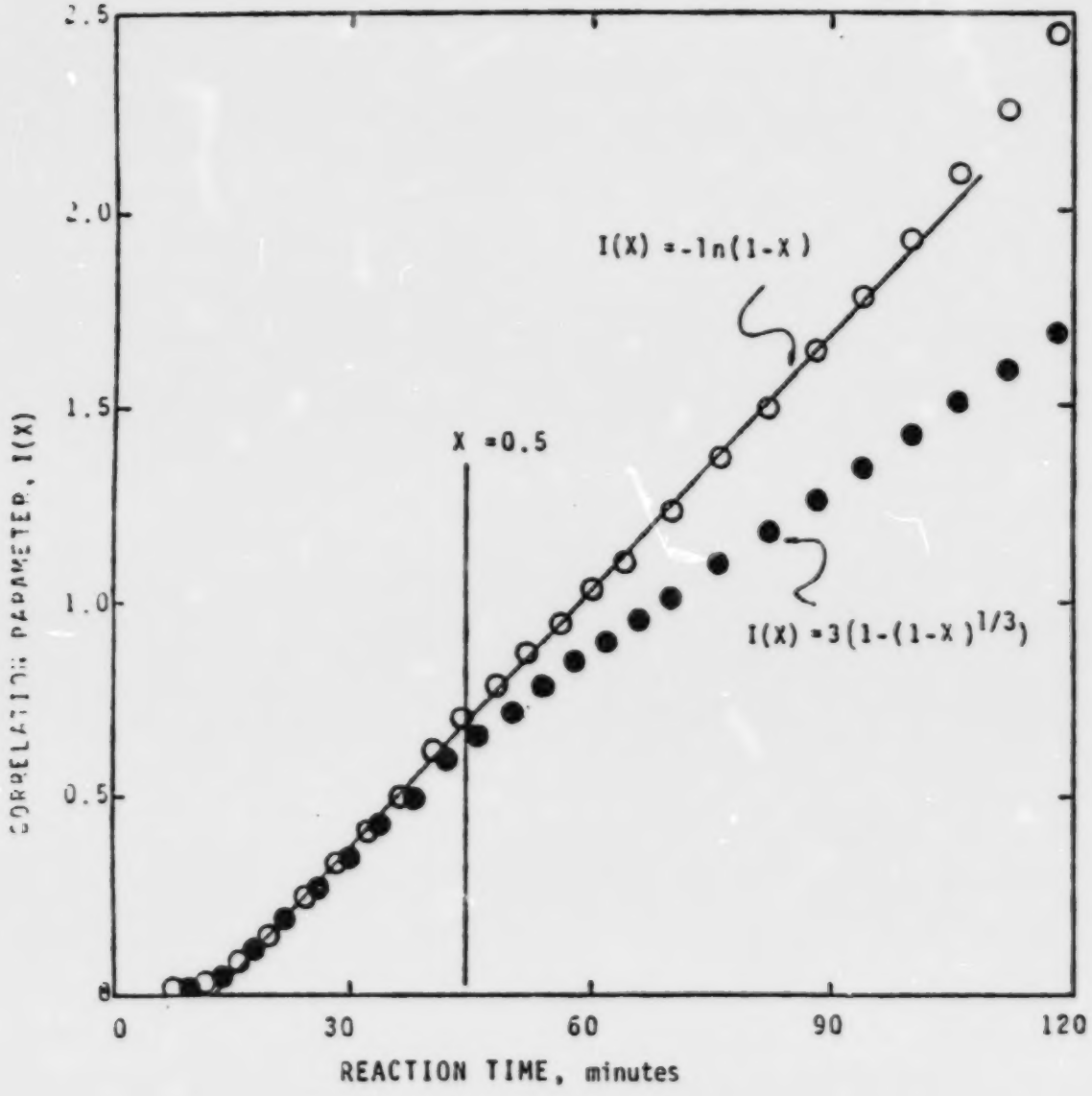

Figure 17. COMPARISON BETWEEN FIRST AND FRACTIONAL ORDER CORRELATION PARAMETERS FOR THE STEAM GASIFICATION OF LIGNITE CHAR

The effect of exchangeable cations on char gasification reactivity was studied using both demineralized and ion exchange enriched lignite samples. The reactivity of individual char samples was defined by the apparent rate constant, k_o or k_1, obtained from the linear portion of the appropriate kinetic plot (i.e. x vs.t, or -ln(1-x) vs.t). A reactivity ratio defined as k/k^*, where k^* is the rate constant for the demineralized char, and k that for the ROM or enriched char, was used to compare the reactivity of chars with different concentrations of calcium and/or sodium ions. Since the catalytic effect of alkali metals varied for steam only and steam/air gasification experiments, the results of these runs are presented in separate sections, which follow.

I. Steam/Char Gasification

First order kinetic plots of carbon conversion vs. time were found to be linear over a carbon conversion range of X = 0.2 to 0.8. Values of the apparent rate constant were determined for each experiment over ranges of similar linearity as that demonstrated in Figure 18. Reactivity ratios were then calculated for ROM and sodium or calcium enriched chars. These values are presented as a function of sodium or calcium concentration in the parent coal in Table 5.

The trend in reactivity ratios indicated the positive catalytic effect of sodium and calcium on the gasification reactivity of lignite chars in steam atmospheres. Initial

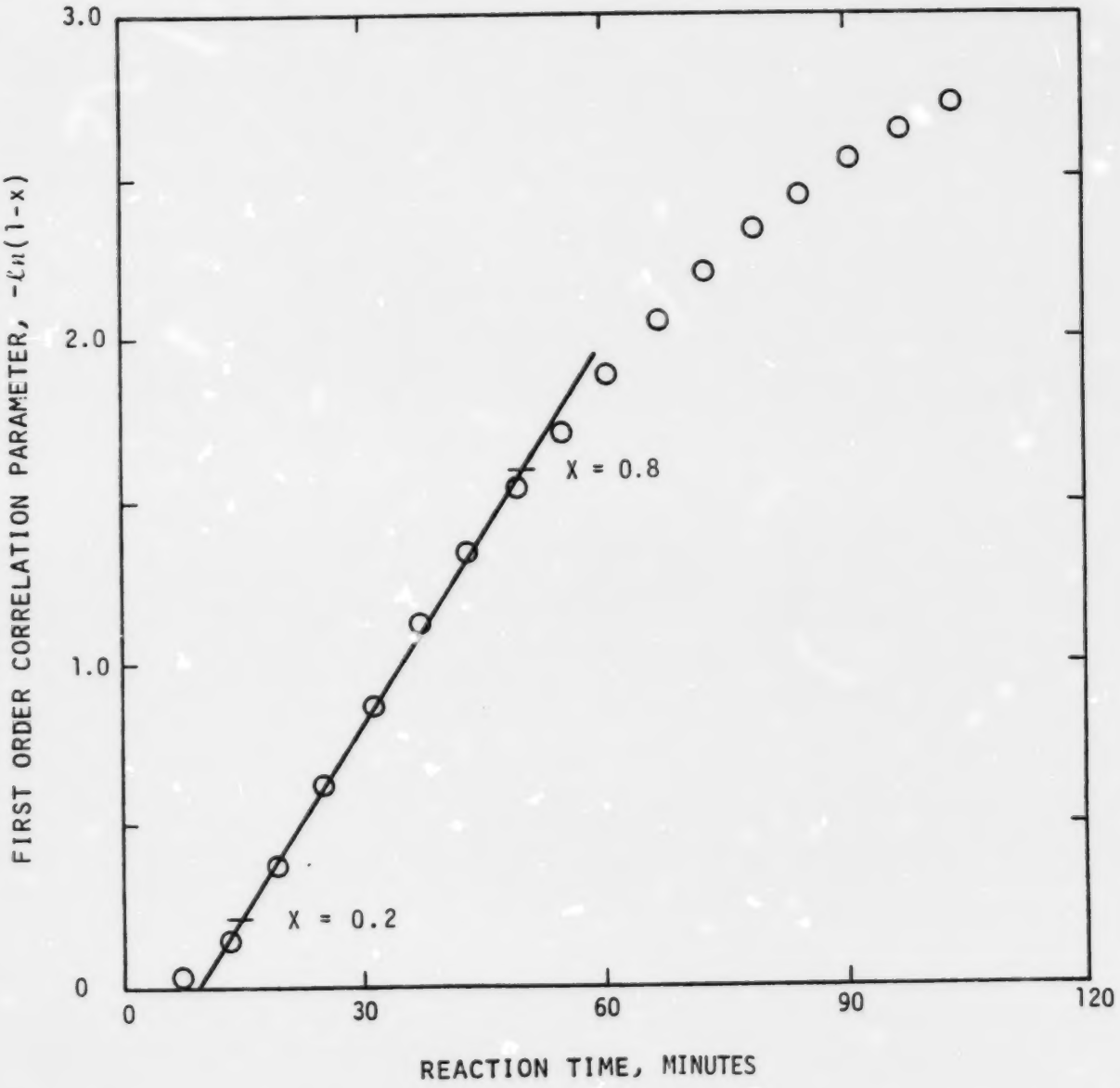

Figure 18. FIRST ORDER KINETICS FOR GASIFICATION OF LIGNITE CHAR IN STEAM

observations also indicated that the catalytic effect of sodium and calcium were similar. The reactivity ratios were plotted versus the sodium or calcium concentration in the parent coal (ROM). Only the ratios obtained from cation-enriched lignite gasification were used in this plot. It was felt the use of ROM coal char gasification data would bias the results as these chars contain, in addition to exchangeable cations of sodium and calcium, other cations, with the ability to influence the reactivity of the char. The results are presented in Figure 19, together with a least squares' fit of the data points. The regression equation resulting from this analysis is:

$$k/k^* = 1.16 + 1.24(Y) \times 10^3 \qquad (12)$$

where Y = concentration of calcium or sodium, moles/g fixed carbon

In order to test the correlation between conversion data for both Coronach and Estevan chars, theoretical conversions based on k values were calculated from equation (12) for the analysis of ROM lignites (Table 5). In both cases predicted conversions were 5 to 20% greater than the actual experimental data. A comparison of theoretical and predicted carbon conversion plots for Estevan lignite char is presented in Figure 20.

Despite the discrepancy of 5 to 20%, explained primarily by sodium and calcium or other active cations present in ROM coals in non-exchangeable form, equation (12) provides a good approximation

TABLE 5. REACTIVITY RATIOS FOR Ca^{++} AND Na^{+} ENRICHED STEAM/CHAR GASIFICATION AT 800°C AND 2MPa

TYPE	Y_{ca}	CATION CONCENTRATION (mole/g FC)X10^3	Y_{na}	REACTIVITY RATIO
Coronach				
ROM		1.26*		1.81
Na(A)			2.86	4.72
Na(B)			2.88	5.74
Na(C)			1.01	3.39
Ca(A)	1.32			2.58
Ca(B)	0.93			2.07
Ca(C)	0.96			2.18
Estevan				
ROM		1.34*		2.60
Na(A)			3.21	4.76
Na(B)			2.65	4.09
Na(C)			0.95	1.55
Ca(A)	2.05			3.21
Ca(B)	0.66			2.36
Ca(C)	1.04			2.57

* Sum of $Y_{ca} + Y_{na}$.

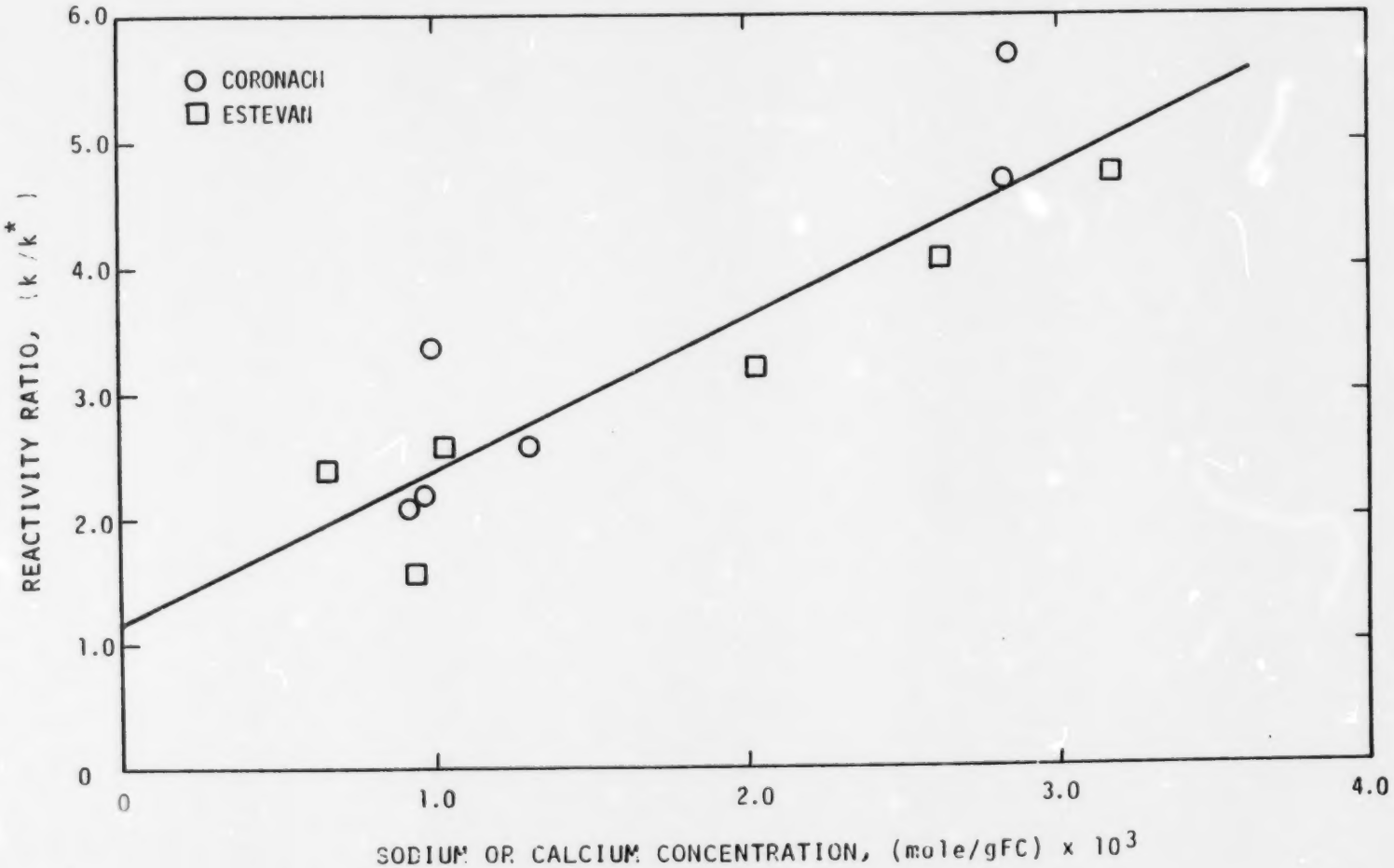

Figure 19. EFFECT OF SODIUM OR CALCIUM CONCENTRATION ON THE REACTIVITY OF ENRICHED LIGNITE CHARS GASIFIED IN STEAM AT 800°C AND 2MPa

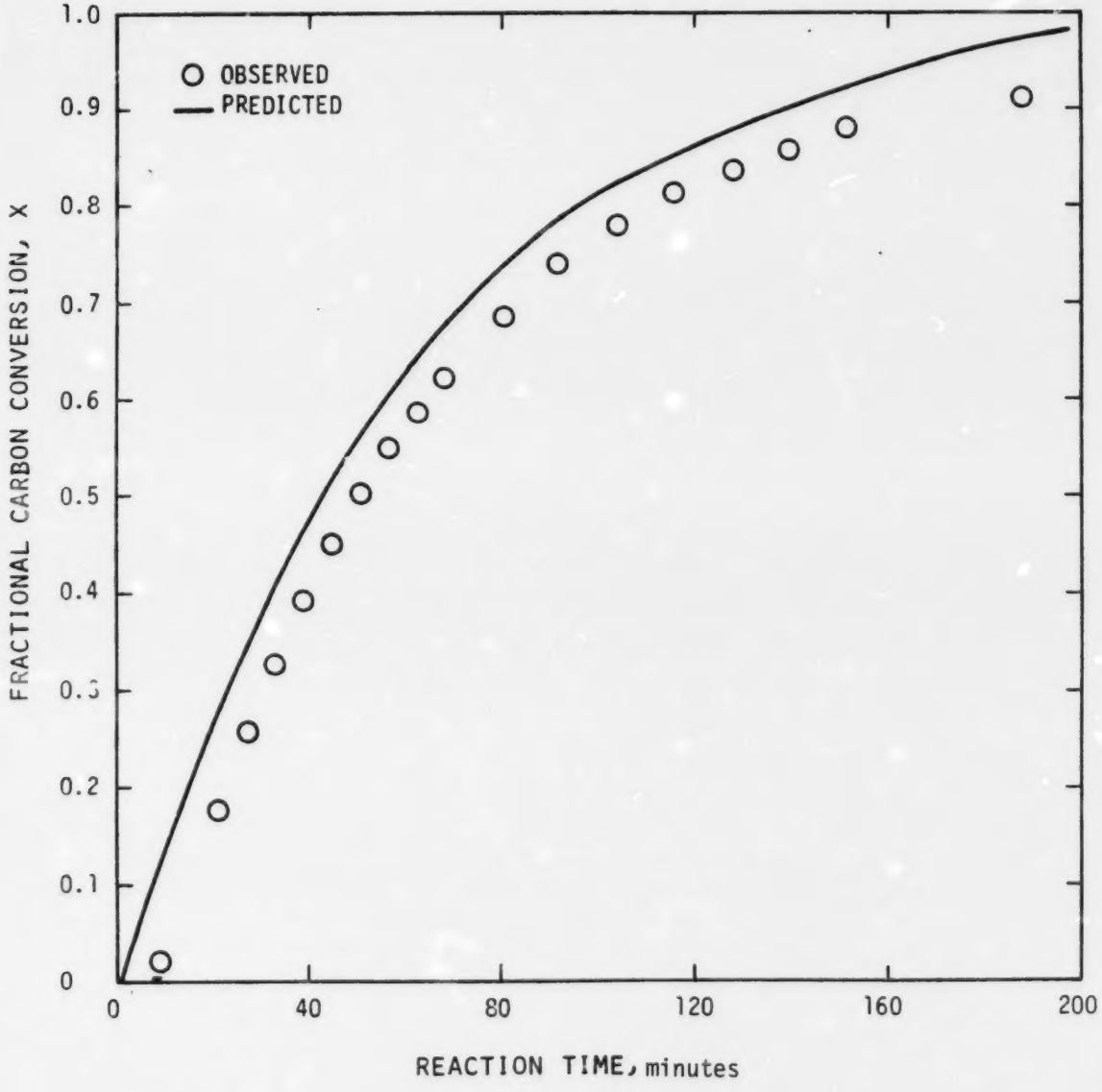

Figure 20. COMPARISON OF OBSERVED AND PREDICTED ROM CARBON CONVERSION FOR THE STEAM GASIFICATION OF LIGNITE CHAR (PREDICTION BASED ON k CALCULATED FROM EQUATION (12))

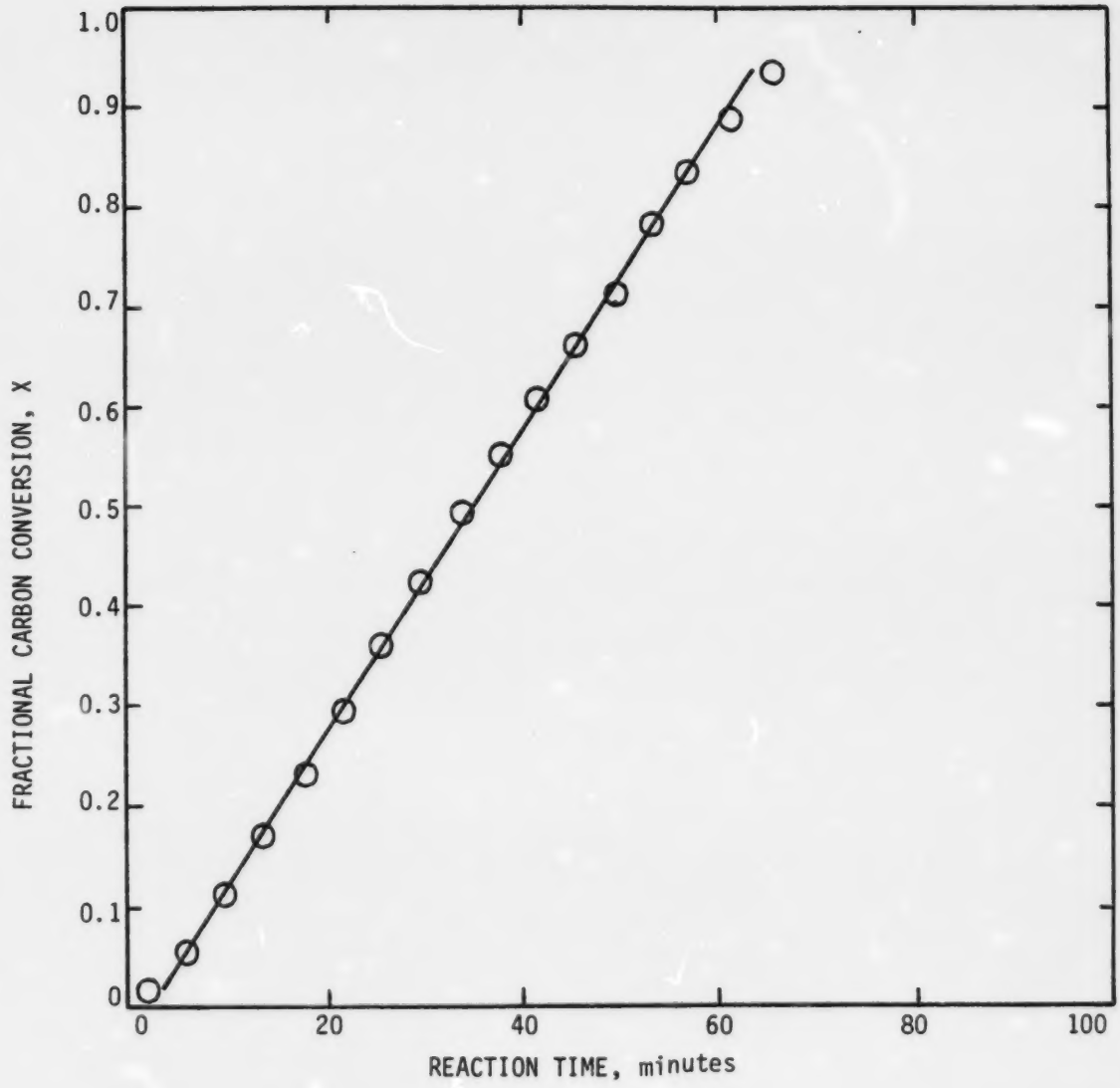

Figure 21. ZERO ORDER KINETICS FOR THE STEAM/AIR GASIFICATION OF ROM CHAR AT 900°C AND 2MPa

of lignite char gasification behaviour. Most importantly it allows quantification of the effects of variation of lignite composition on lignite gasification behaviour.

II. Steam/Air Gasficiation of Lignite Char

Zero order kinetic plots of steam/air gasification carbon conversion data were found to be linear over a carbon conversion range of X = 0.1 to 0.9 (Figure 21). Apparent rate constants were determined for each experiment and reactivity ratios (k/k^*) calculated. These values are presented in Table 6.

The trend of the reactivity ratios indicates the positive catalytic effect of alkali metal cations in the gasification reactivity of lignite ROM chars at 0.1 MPa only. The reactivity ratios for experiments conducted at 2MPa are very close to 1. Hence the catalytic activity of the alkali metal cations is no longer evident. This does not indicate the absence of any catalytic activity; however, under the conditions at which these experiments were performed, a change in the reaction mechanism is possible, with an associated change in reaction rate. No corresponding change in reaction order has been observed, however.

For temperatures achieved in most gasifiers, it is probable that the combined effects of pore diffusion and chemical reaction

TABLE 6. KINETIC PARAMETERS FOR THE STEAM/AIR GASIFICATION OF ROM AND ACID-WASHED CHARS

CHAR TYPE	TEMPERATURE (°C)	PRESSURE (MPa)	k X 10^2 (min^{-1})	REACTIVITY RATIO k/k*
		Coronach		
ROM	800	0.1	1.538	2.167
ROM	900	0.1	1.975	1.778
ROM	800	2.0	1.500	0.907
ROM	900	2.0	1.633	0.988
A-W	800	0.1	0.710	
A-W	900	0.1	1.111	
A-W	800	2.0	1.653	
A-W	900	2.0	2.049	
		Estevan		
ROM	800	0.1	1.528	1.852
ROM	900	0.1	1.909	1.850
ROM	800	2.0	1.434	
ROM	900	2.0	1.621	0.904
A-W	800	0.1	0.825	
A-W	900	0.1	1.032	
A-W	800	2.0	1.313	
A-W	900	2.0	1.794	

will control the overall reaction rate. The best approach, therefore, will be to compare the data with those derived by direct experimentation using the same char, temperature and pressure conditions or those closest to the desired conditions.

Environmental Effects of Gasification of Saskatchewan Lignites

The composition of condensates collected during the gasification of Saskatchewan lignite coals compares well with the composition of gasifier sluice water and quench water obtained from large-scale fixed-bed gasifiers. Comparison of heavy element concentrations with concentrations allowable under the Canadian Drinking Water Objectives and the U.S. Standards shows that only those for arsenic, boron, and chromium are exceeded. The high chromium levels are thought to arise from the Hastelloy reactor material due to a high surface area to volume ratio in bench scale reactors. Indeed chromium concentrations in the Wellman-Galusha (Ft. Snelling) gasifier ash sluice water and cyclone dust quench water are an order of magnitude below the Canadian Drinking Water objectives and American primary standard.

The higher arsenic and boron levels are thought to be directly related to their high levels in the Canadian lignites . Arsenic shows low toxicity to plant, animal and aquatic life forms and its major threat is likely to the micro-organism used in the

biox treatment facilities.

The organic content of the condensate is similar to that observed for other fixed-bed gasifiers. The average phenol/TOC ratio of 0.83 for all runs is in good agreement with the ratio of 0.82 obtained for the slagging fixed-bed gasifier at the Grand Forks Research Centre. The phenol/TOC ratios for the Synthane PDU and Hygas gasification facilities are 0.265 and 0.292 respectively.

Elements such as mercury, selenium, lead, fluorine, and antimony show no enrichment in the ash residue as compared to their levels in the parent coal. This indicates a high degree of volatility for these elements. Arsenic does not show this anticipated effect. The only potential environmental problems associated with gasifier ash are those of leaching and are similar in nature to those encountered in ash disposal from conventional coal fired facilities.

CONCLUSIONS

Reactor design criteria for commercial coal gasifiers are largely dependent on coal char reactivity. Lignite char (especially from Saskatchewan lignites) possesses a higher gasification reactivity than higher rank coals due to the presence of naturally occurring alkali metals such as calcium and sodium, which exhibit high catalytic reactivity.

Regarding reaction order, it was determined that air-only gasification of char exhibited first order kinetics at low air feedrates, with a shift to zero order at higher flowrates. Steam-only gasification proceeded according to first order kinetics with respect to carbon conversion, while steam/air char gasification demonstrated zero order behaviour. A fractional order kinetic model proposed by Nandi and Johnson (1979) provided a poorer fit of the experimental data generated in Phases I to IV.

In the present Phase (V) an APL computer language program has been developed to reduce all data to a common base. The most important kinetic expression developed as a result of this data reduction is the following:

$$k/k^* = 1.16 + 1.24(Y) \times 10^3$$

where Y is the concentration of calcium or sodium in the lignite, in moles per gram fixed carbon, and k, k^* are the apparent rate constants for the cation-enriched and acid-washed lignites, respectively.

The importance of this regression equation is that it permits the prediction of the extent and rate of the char/steam reaction, and, when combined with other information such as air flowrates, etc., it allows the design of a gasification reactor based on chemical reaction engineering principles.

The commercial significance of this design equation is that, based on a reduced number of experiments, a potential lignite gasification operation may be designed. Of course, feasibility and market studies would also be required.

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APPENDIX

COMPUTER PROGRAMS USED IN THE

EVALUATION OF DATA

```
      DESCRIBE

  THIS IS A COLLECTION OF  APL  FUNCTIONS WHICH HAVE BEEN
USED TO GENERATE DATA FOR PHASES I THRU V. THE FUNCTIONS
ARE GROUPED INTO DIFFERENT WORKSPACES, ONE FOR EACH PHASE.
  THE FUNCTIONS CALCULATE THE CARBON CONVERSION VERSUS TIME
OR NORMALIZED TIME PARAMETER TAU.  THE INPUT TO EACH FUNCTION
SET DEPENDS ON THE PROGRAM PHASE. PHASES  I  AND  II  USE THE
GAS COMPOSITION OBTAINED FROM GAS CHROMATOGRAPHIC ANALYSIS,
WHILE PHASES  III  AND  IV  USE THE VOLTAGE LEVEL OUTPUTS
FROM THE INFRARED ANALYZERS USED FOR ANALYSIS OF THE OFF GAS.
MORE DETAILED INFORMATION IS PROVIDED IN EACH OF THE FOLLOW-
ING  INFO  FUNCTIONS:

WORKSPACEINFO      HOW TO STORE THE FUNCTIONS IN SEPARATE WORK-
                   SPACES.

GLOBALINFO         A LIST OF GLOBAL VARIABLES WHICH MUST EXIST
                   WITHIN EACH WORKSPACE.

PROGRAMMERINFO     SOME INFORMATION ON THE STRUCTURE OF THE
                   FUNCTIONS.

ENTERINFO          HOW TO ENTER DATA AND USE THE FUNCTIONS.


      WORKSPACEINFO

   THE GROUPS  PHASEI, PHASEII, PHASEIII AND PHASEIV WERE
USED FOR ENTRY OF THE RESPECTIVE DATA COLLECTED FOR EACH OF
THESE PHASES
   THE DATA FOR PHASES I  AND II WERE TAKEN FROM REPORTS I
AND II.  THE DATA FOR PHASES III AND IV WERE IN THE FORM OF
OUTPUT VOLTAGES FROM THREE RIKEN INFRARED GASANALYZERS.
   GROUP  KINETICS  WAS USED TO GENERATE CARBON CONVERSION
DATA FOR ALL PHASES.  GROUP GRAPH CAN BE USED TO PLOT DATA
FOR ALL GROUPS.
   THE MEMBERS FOR EACH GROUP ARE LISTED UNDER GLOBALINFO.
```

GLOBALINFO

THE FOLLOWING GLOBAL VARIABLES AND GROUP NAMES MUST EXIST IN YOUR WORKSPACE BEFORE ATTEMPTING TO EXECUTE THE FUNCTIONS

PHASEI — A GROUP NAME CONTAINING ALL FUNCTIONS FOR DATA ENTRY FROM PHASE I REPORT. THE MEMBERS OF THIS GROUP ARE:
NEW READ CHANGEDATA CHANGETIME INSERT

PHASEII — A GROUP NAME CONTAINING ALL FUNCTIONS FOR DATA ENTRY FROM PHASE II REPORT. THE GROUP MEMBERS ARE THOSE OF PHASEI.

PHASEIII — A GROUP NAME CONTAINING ALL FUNCTIONS FOR DATA ENTRY FROM PHASE III REPORT. THE GROUP MEMBERS ARE:
INPUT READ INSERT ENDTIME CO CO2 CH4 ICO ICO2 ICH4 CHANGE TIME REFINE

PHASEIV — A GROUP NAME CONTAINING ALL FUNCTIONS FOR DATA ENTRY FROM PHASE IV. THE GROUP MEMBERS ARE THOSE FOR PHASEIII.

KINETICS — A GROUP NAME CONTAINING ALL FUNCTIONS FOR CONVERSION CALCULATIONS. THE MEMBERS OF THIS GROUP ARE:
CARBON CONVERSION READ INTERPOLATE CHOP CALC RATE REFINE

GRAPH — A GROUP NAME CONTAINING ALL FUNCTIONS FOR PLOTTING CONVERSION VERSUS TIME DATA. THE FUNCTIONS APPLY A NATURAL CUBIC SPLINE CURVE SMOOTHING TECHNIQUE. THE MEMBERS OF THIS GROUP ARE:
PLOT PLOTCOORD SPLINECALC SPLINEVAL

DATA — A MATRIX CONTAINING THE RAW DATA WHEN ENTERED FOR PHASES III AND IV. THE NUMBER OF ROWS IS EQUAL TO THE NUMBER OF OBSERVATIONS MADE. THE COLUMNS ARE:
DATA[;1] THE SAMPLE TIMES
DATA[;2] THE IR READOUTS FOR CO
DATA[;3] THE IR READOUTS FOR CO2
DATA[;4] THE IR READOUTS FOR CH4
DATA[;5] THE CUMULATIVE GAS VOLUME PRODUCED AT TIME DATA[;1]. IF NO CH4 DATA ARE AVAILABLE DATA[;4] CONTAINS THE CUMULATIVE GAS VOLUME.

M — MATRIX CONTAINING GAS COMPOSITION IN VOLUME PERCENT. THE ROWS AND COLUMNS ARE IDENTICAL TO THOSE IN DATA.

PROGRAMMERINFO

THE FOLLOWING IS A LISTING OF ALL FUNCTIONS USED IN THE VARIOUS WORKSPACES. THIS INFO SECTION WILL PROVIDE A SHORT DESCRIPTION OF EACH FUNCTION. ALL FUNCTIONS ARE WORKING FUNCTIONS AND NO COMMENTS ON PROGRAMMING STYLE OR ALGORITHMS WILL BE PROVIDED.

CALC M	CALCULATES THE FRACTIONAL CONVERSION, AND THE CORRELATION PARAMETERS 3(1-(1-X)*1/3) AND LN(1-X) VERSUS TIME. THE FUNCTION REQUIRES THE EXISTENCE OF MATRIX M. THE FUNCTION REQUESTS THE INPUT FOR WEIGHT AND MOISTURE CONTENT OF THE COAL, THE CARBON CONTENT OF THE ASH RESIDUE, AND THE ASH CONTENT OF THE COAL. THE MAIN USE IS FOR PHASE IV TYPE CALCULATIONS.
CARBON	CALCULATES THE TOTAL AMOUNT OF CARBON GASIFIED FROM THE CO, CO2 AND CH4 CONTENT IN THE OFF-GAS. THE FUNCTION REQUESTS INPUT FOR THE STATION PRESSURE AND TEMPERATURE.
CH4	CONTAINS THE COLUMN NUMBER FOR CH4 IN MATRICES DATA AND M.
CHANGE	ALLOWS CORRECTION OF ERRORS DURING DATA ENTRY FOR PHASES III AND IV.
CHANGEDATA	ALLOWS CORRECTION OF ERRORS DURING DATA ENTRY FOR PHASES I AND II.
CHANGETIME	ALLOWS CORRECTION TO A TIME ENTRY DURING DATA ENTRY FOR PHASES I AND II.
CHOP	USES LOGICAL VARIABLE VECT TO REDUCE OUTPUT FOR PHASE III AND IV DATA.
CO	CONTAINS THE COLUMN NUMBER FOR CO IN MATRICES DATA AND M
CO2	CONTAINS THE COLUMN NUMBER FOR CO2 IN MATRICES DATA AND M.
CONVERSION	CALCULATES THE HALFTIME FOR PHASES III AND IV. THE FUNCTION REQUESTS THE INPUT FOR STATION PRESSURE AND TEMPERATURE, VOLATILE MATTER AND ASH CONTENT OF THE COAL, WEIGHT AND MOISTURE CONTENT OF THE COAL, AND CARBON CONTENT OF THE ASH RESIDUE.

ENDTIME	*CALCULATES ENDTIMES FROM THE START TIME AND DURATION OF THE RUN FOR PHASE III DATA.*
ICH4	*SPAN VALUE FOR CH4 IR GAS ANALYZER.*
ICO	*SPAN VALUE FOR CO IR GAS ANALYZER.*
ICO2	*SPAN VALUE FOR CO2 IR GAS ANALYZER.*
INPUT	*USED FOR ENTERING PHASE III AND IV DATA.*
INSERT M	*ALLOWS INSERTION OF OMITTED DATA POINTS INTO MATRICES M OR DATA FOR PHASES I,II,III AND IV.*
NEW	*CREATES A NEW DATASET FOR PHASES I AND II DATA.*
PLOT COL	*PLOTS ANY DATA COMBINATION VERSUS TIME,OF MATRICES DATA, M AND MM. COL INDICATES THE COLUMN NUMBER TO BE PLOTTED VERSUS THE TIME AXIS IN COLUMN 1.*
X PLOTCOORD Y	*PLOTS X VERSUS Y. CALLED FROM PLOT.*
QUADFIT	*CALCULATES A QUADRATIC FIT USING ANY COMBINATION OF COLUMNS IN MATRICES DATA, M AND MM.*
RATE	*CALCULATES HALFTIMES FOR PHASE I,II,III AND IV. THE FUNCTION REQUESTS INPUT FOR STATION PRESSURE AND TEMPERATURE, WEIGHT AND MOISTURE CONTENT OF THE COAL AND CARBON CONTENT OF THE ASH RESIDUE. THIS FUNCTION WAS MAINLY USED IN PHASE III AND IV CALCULATIONS.*
READ	*USED IN THE MAJORITY OF FUNCTIONS FOR DATA ENTRY.*
REFINE	*MAKES ZERO AND SPAN DRIFT CORRECTIONS TO IR READINGS COLLECTED DURING PHASE III AND IV.*
RUN	*CALCULATES RATE DATA FOR PHASE III AND IV. CALLS REFINE AND RATE.*
X SPLINECALC Y *X SPLINEVAL C*	*FUNCTIONS FOR EVALUATION OF NATURAL CUBIC SPLINES.*
TIME M	*DELETE A ROW OF DATA FROM MATRICES DATA, M AND MM.*

ENTERINFO

ALL FUNCTIONS ARE SELF EXPLANATORY AND WILL REQUEST THE TYPE OF DATA REQUIRED FOR INPUT. WHERE LONG DATA ENTRY SESSIONS ARE REQUIRED SUCH AS WHEN ENTERING RAW DATA, THE FUNCTIONS WILL PERFORM SOME EDITING AND CHECKING TO FACILITATE SMOOTH DATA ENTRY AND REDUCE THE NEED FOR SUBSEQUENT EDITING. A DESCRIPTION OF EACH FUNCTION IS GIVEN IN PROGRAMMER INFO.

```
      ∇ CALC M ;MM;V;C;P;COR;AVC;DLTVOL;W;MO;FC;ASH;CA;HT
[1]   C←2 3 4
[2]   COR←1000
[3]   MM←(⍴ M)⍴ 0
[4]   MM←(P←0,(¯1+(⍴ M)[1])⍴ 1)/[1]MM
[5]   V←5
[6]   DLTVOL←(¯1 ↓ ,(1 ⌽1 M[;V])-M[;V])×COR
[7]   AVC←+/[2]((¯1 0)↓ M[;C]+1 ⌽1 M[;C])÷200
[8]   'ENTER THE WEIGHT AND MOISTURE CONTENT OF THE COAL'
[9]   W←⌈/C←READ
[10]  MO←0.01×⌊/C
[11]  CA←0.01×CA←¯1 ↓ ⎕,⍴ ⎕←'ENTER THE CARBON CONTENT OF THE
 ASH RESIDUE'
[12]  ASH←0.01×ASH←¯1 ↓ ⎕,⍴⎕←'ENTER THE ASH CONTENT OF THE C
OAL'
[13]  CDAF←(W×(1-MO))×CA×ASH
[14]  MM[;1]←P/[1](M[;1])
[15]  MM[;2]←+\FRACT←CA←CDAF←(+/FRACT←DLTVOL× .TP AVC×12×
      4.2293E¯2  )
[16]  MM[;3]←(1-(1-MM[;2])*÷3)×3
[17]  MM[;4]←-(●(1-MM[;2]))
[18]  MM[;5]←MM[;1]+HT←(⌽[2](1 1 0 0 0)/[2]MM) INTERPOLATE
      0.5
[19]  'ENTER TITLE'
[20]  TITLE←⍞
[21]  'PREPARE PRINTER'
[22]  C←⎕
[23]  TITLE
[24]  'THE TOTAL AMOUNT OF CARBON AT START OF GASIFICATION
';CA
[25]  'HALF TIME      ';HT
[26]  'TIME     X    3(1-(1-X)*÷3)  LN(1-X)    1/T'
[27]  MM
      ∇


      ∇ Z←CO
[1]   Z←3
      ∇


      ∇ Z←CO2
[1]   Z←2
      ∇


      ∇ Z←CH4
[1]   Z←4
      ∇
```

```
      ∇ CARBON ;COR;PRESS;TEMP;AVC;DLTVOL;MM;C;FRACT
[1]   MM←((C←1 ↑ ⍴ M),2).R 0
[2]   M←(0,C ⍴ 1)\[1]M
[3]   'ENTER THE STATION PRESSURE IN KPA'
[4]   PRESS←⍞
[5]   'ENTER THE STATION TEMPERATURE IN DEG C'
[6]   TEMP←273.2+⍞
[7]   COR←(101.32 ÷ 273.2)×(TEMP ÷ PRESS)
[8]   DLTVOL←(¯1 ↓(1 ⌽ M[;4])-M[;4])×COR
[9]   AVC←+/[2]((¯1 0 ↓ M[;2 3]+1 ⌽ M[;2 3])÷200)
[10]  MM[;2]←+\FRACT ÷(C←+/FRACT←DLTVOL× ⍉ AVC×12÷4.2293E¯2
      )
[11]  MM[;1]←¯1 ↓ M[;1]×2
[12]  C
[13]  M←1 0 ↓ MM
      ∇


      ∇ Z←CHANGE ;L;ROWS;COLS;N;T;K;NEEDED
[1]   T←DATA[1;2 3]
[2]   COLS←(⍴ DATA)[2]
[3]  STARTROW: L←⍳ 0
[4]  RETRY: 'ENTER TIME BETWEEN ';24 60 ⍕(⌊/T);' AND ';24
      60 ⍕(⌈/T)
[5]  MORE: L←L,,⍞
[6]   NEEDED←¯1+COLS-⍴ L
[7]   → (0=NEEDED)/NEXTROW
[8]   → (NEEDED<0)/BADROW
[9]   'GIVE ';NEEDED;'MORE VALUES'
[10]  → MORE
[11] BADROW: 'YOU GAVE ';-NEEDED;' EXTRA VALUES. START ENTRI
ES FOR THIS TIME OVER AGAIN'
[12]  → STARTROW
[13] NEXTROW: DATA[N;]←(N-1),L
      ∇


      ∇ Z←ICH4
[1]   Z←13.5
      ∇


      ∇ Z←ICO
[1]   Z←35
      ∇


      ∇ Z←ICO2
[1]   Z←35
      ∇
```

```
      ∇ CHANGEDATA ;L;ROWS;COLS;N;T;NEEDED;LOC
[1]   'ENTER THE DATASET NAME'
[2]   X←⍞
[3]   DATA←⍳ 0
[4]   ⍎'DATA←',X
[5]   ROWS←(⍴ DATA)[1]
[6]   L←⍳ 0
[7]  RETRY: 'ENTER THE TIME BETWEEN  ';DATA[1;1];'  AND  ';
DATA[ROWS;1]
[8]   T←,⎕
[9]   → (1=⍴ T)/L1
[10]  'YOU MUST ENTER ONE VALUE ONLY. TRY AGAIN'
[11]  → RETRY
[12] L1: → (T ∈ DATA[;1])/GOODTIME
[13]  'THIS IS AN INVALID TIME FOR THIS DATA SET.'
[14]  'THIS FUNCTION IS FOR DATA CORRECTION ONLY'
[15]  → ('E'=(⍞,⎕←'ENTER EXIT OR LIST')[1])/0
[16]  'THE VALID TIMES FOR THIS DATA SET ARE: ';DATA[;1]
[17]  → RETRY
[18] GOODTIME: LOC←1 +((T=DATA[;1])/⍳ ROWS),0
[19]  'ENTER DATA FOR TIME   ';T
[20] MORE: L←L,,⎕
[21]  NEEDED←¯1+(⍴ DATA)[2]-⍴ L
[22]  → (0=NEEDED)/NEXTROW
[23]  → (NEEDED<0)/BADROW
[24]  'GIVE   ';NEEDED;'  MORE VALUES'
[25]  → MORE
[26] BADROW: 'YOU GAVE  ';-NEEDED;'  EXTRA VALUES'
[27]  'ENTER DATA FOR THIS TIME PERIOD AGAIN'
[28]  → GOODTIME
[29] NEXTROW: N←DATA[LOC;]
[30]  DATA[LOC;2 3 4 5]←L
[31]  'OLD DATA   ';N
[32]  'REPLACED BY ';DATA[LOC;]
[33]  'THE DATA SET IS NOW: '
[34]  ⍎ X,'←DATA'
      ∇


      ∇ Z←CHOP
[1]   Z←((¯1 ↓ ⍴ MM)⍴ VECT)
      ∇
```

```
      ∇ C[illegible];L;LOC;T;NEEDED
[1]   'E[illegible]T NAME'
[2]   X←
[3]   ∈'[illegible]',X
[4]   'THE CURRENT TIME ENTRIES FOR THIS DATA SET ARE:  ';
DATA[;1]
[5]   L←⍳ 0
[6]  RETRY: 'ENTER OLD TIME'
[7]   T←,⎕
[8]   → (1=⍴ T)/L1
[9]   'YOU MUST ENTER ONE VALUE ON;Y. TRY AGAIN'
[10] L1: → (T ∈ DATA[;1])/GOODTIME
[11]  → RETRY
[12] GOODTIME: LOC←1 +((T=DATA[;1])/⍳(⍴ DATA)[1]),0
[13]  DATA[LOC;]←0
[14]  'THE DATA FOR TIME  ';T; ' HAS BEEN REMOVED FROM THE D
ATASET'
[15]  → ('Y'=(⍞,⎕←'DO YOU WANT TO REPLACE THIS DATA?')[1])/
CONT
[16]  DATA=(DATA ∨.≠ 0)/[1]DATA
[17]  → 0
[18] CONT: 'ENTER NEW TIME AND DATA'
[19] MORE: L←L,,⎕
[20]  NEEDED←(⍴ DATA)[2]- ⍴ L
[21]  → (0=NEEDED)/NRXTROW
[22]  → (NEEDED<0)/BADROW
[23]  'GIVE  ';NEEDED;' MORE VALUES'
[24]  → MORE
[25] BADROW: 'YOU GAVE  ';-NEEDED;'  EXTRA VALUES, REENTER A
LL PARAMETERS'
[26]  → CONT
[27] NEXTROW: DATA[LOC;]←L
[28]  'DATA REPLACED'
[29]  ∈ X,'←DATA'
      ∇


      ∇ Z←ENDTIME ;TS;D
[1]   'ENTER START TIME'
[2]   TS←,⎕
[3]   'ENTER DURATION'
[4]   D←⎕
[5]   'ENDTIME'
[6]   Z←24 60 ⊤ (D +6↑24 60 ⊥ TS)
      ∇
```

```
      ∇ CONVERSION ;COR;P;T;AVC;DLTVOL;C;V;CR;ASH;FRACT;MM;
VM;W0;DLTW
[1]   M←(M∧ .>0)/[1]M
[2]   MM←((C←1 ↑ ⍴ M),5)⍴ 0
[3]   M←(0,C ⍴ 1)\[1]M
[4]   V←(¯1 ↑ ⍴ M)
[5]   C←1+⍳ V - 2
[6]   'ENTER THE STATION PRESSURE IN KPA'
[7]   P←⍞
[8]   'ENTER THE STATION TEMPERATURE IN DEG C'
[9]   T←273.2+⍞
[10]  COR←(101.32÷288.2)×(T÷P)
[11]  DLTVOL←(¯1 0 ↑,(1 ⌽ 1 M[;V])-M[;V])×COR
[12]  AVC←+/[2]((¯1 0 ↑ M[;C]+1 ⌽ M[;C])÷200)
[13]  'ENTER VOLATILE MATTER AND ASH CONTENT OF THE COAL'
[14]  VM←0.01×(⌈/C←READ)
[15]  ASH←0.01×(⌊/C)
[16]  'ENTER WEIGHT AND MOISTURE CONTENT OF THE COAL'
[17]  W0←C -(C←⌈/C)×0.01×(⌊/C←READ)
[18]  'ENTER THE CARBON CONTENT OF THE RESIDUE'
[19]  CR←0.01×⍞
[20]  MM[;2]←+\FRACT÷(C←+/FRACT←DLTVOL×.TS VAC×12×4.2293E¯2
      )
[21]  'TOTAL CARBON GASIFIED ';C
[22]  VM←(DLTW←W0 -(C←W0×ASH×(1+CR)))÷W0
[23]  DLTW←DLTW++\FRACT
[24]  MM[;3]←((DLTW÷W0)-VM)÷(1-VM+SAH)
[25]  MM[;4]←(1-(1-MM[;3])*÷3)×3
[26]  MM[;1]←¯1 ↑ M[;1]
[27]  MM[;5]←MM[;1]+C←(⌽[2](5 ⍴ 1 1 0 0 0)/[2]INTERPOLATE
      0.5
[28]  'THE T0.5 VALUE FOR THIS RUN IS ';C
[29]  M←1 0 ↑ MM
      ∇


      ∇ INSERT M ;DV;C
[1]   DV←1,(1 ↑ ⍴ M)⍴ 1
[2]   'ENTER TWO NUMBERS BETWEEN WHICH INSERTION IS TO TAKE
PLACE'
[3]  L1: → (1=((⌈/C)-⌊/C←READ))/L2
[4]   'THE NUMBERS MUST BE CONSECUTIVE'
[5]   → L1
[6]  L2: DV[(⌈/C)+1]←0
[7]   DATA←DV\[1]M
[8]   DATA[;1]←0,⍳((⍴ DV)-1)
      ∇
```

```
      ∇ Z←INPUT ;ROWS;COLS;N;NEEDED
[1]   'ENTER THE START AND FINISH TIMES, IN HOURS AND MINUTE
S'
[2]   L1: T←,T←⍞
[3]    → (4=⍴ T)/L2
[4]    'YOU MUST ENTER FOUR VALUES. TRY AGAIN'
[5]    → L1
[6]   L2: T←24 60 ⊥ .TP(2 2 ⍴ T)
[7]    L←(0.5×((⌈ /T)- ⌊ /T)),5
[8]    Z←L ⍴ 0
[9]    ROWS←L[1]
[10]   COLS←L[2]
[11]   Z[;1]←0, ¯1 + L[1]
[12]   Z[1;2 3]←T
[13]   N←2
[14]  STARTROW: L←⍳ 0
[15]  RETRY: 'ENTER TIME';24 60 ⍉ (⌊ /T)+2×N
[16]  MORE: L←L,,⍞
[17]  NEEDED: →¯1+COLS - ⍴ L
[18]   → (0=NEEDED)/NEXTROW
[19]   → (NEEDED<0)/BADROW
[20]   'GIVE';NEEDED;' MORE VALUES'
[21]   → MORE
[22]  BADROW: 'YOU GAVE ';-NEEDED;' EXTRA VALUES. START ENTRI
ES FOR THIS TIME OVER AGAIN'
[23]   → STARTROW
[24]  NEXTROW: Z[N;]←(N-1),L
[25]   → (ROWS ≥ N←N+1)/STARTROW
[26]   DATA←Z
       ∇


      ∇ Z←TIME M ;K
[1]    Z←⍳ 0
[2]    K←24 60 ⊥ 2 ↑ M
[3]    → (~(K=⌊ K)∧(K ≥ ⌊/T)∧ K ≤ ⌈/T)/L2
[4]    → (0=⍴ L)/L1
[5]    ⍴ L;'VALUE DESTINED FOR TIME ';M;' DISCARDED'
[6]   L1: L=⍳ 0
[7]    N←0.5×(24 60 ⊥ 2 ↑ M)-⌊/T
[8]    'OK TIME ';M
[9]    → 0
[10]  L2: 'INVALID TIME. TRY AGAIN'
       ∇
```

```
      ∇ Z←READ ;C
[1]   L1: C←,C←⍞
[2]    → (2=⍴ C)/L2
[3]    'YOU MUST ENTER TWO VALUES TRY AGAIN'
[4]    → L1
[5]   L2: Z←C
      ∇


      ∇ NEW ;L;COLS;N;V;NEEDED;Z
[1]    'ENTER THE NEW DATASET NAME'
[2]    X←⍞
[3]    Z←1 5 ⍴ 0
[4]    COLS←5
[5]    'ENTER MINUTES FROM START, ENTER 99 FOR END OF DATA'
[6]   NEXTTIME: 'ENTER TIME'
[7]   L1: T←,⍞
[8]    → (999 ∈ T)/DONE
[9]    → (1=⍴ T)/STARTROW
[10]   'YOU MUST ENTER  O N E   VALUE ONLY. TRY AGAIN'
[11]   → L1
[12] STARTROW: L←⍳ 0
[13] RETRY: 'ENTER DATA FOR TIME  ';T
[14] MORE: L←L,,⍞
[15]   NEEDED← ¯1+COLS - ⍴ L
[16]   → (0=NEEDED)/NEXTROW
[17]   → (NEEDED<0)/BADROW
[18]   'GIVE  ';NEEDED;'  MORE VALUES'
[19]   → MORE
[20] BADROW: 'YOU GAVE  ';-NEEDED;' EXTRA VALUES. START ENTR
IES FOR THIS TIME OVER AGAIN'
[21]   → STARTROW
[22] NEXTROW: Z←Z,[1]V←T,L
[23]   → NEXTTIME
[24] DONE: DATA←Z
[25]   ∈ X,'←DATA'
      ∇


      ∇ Z←T INTERPOLATE A ;I
[1]    I←+/A>T[;1]
[2]    Z←T[I;2]+(A-T[I;1])×(T[I+1;2]-T[I;2])÷(T[I+1;1]-T[I;
       1])
      ∇
```

```
      ∇ RATE ;MM;V;C;P;COR;AVC;DLTVOL;W;MO;FC;ASH;CA;HT;I
[1]   M←(M∧.>0)/[1]M
[2]   MM←((C←1 ↑ ⍴ M),5)⍴ 0
[3]   M←(0,C ⍴ 1)\[1]M
[4]   V←(¯1 ↑⍴ M)
[5]   R←(¯1 ↑⍴ M)
[6]   C←2 3
[7]   'ENTER STATION PRESSURE IN KPA '
[8]   P←⍞
[9]   'ENTER STATION TEMPERATURE IN DEG C'
[10]  T←273.2+⍞
[11]  COR←(101.32÷288.2)×(T÷P)
[12]  DLTVOL←(¯1 ↓ I←,I← (1 ⊖ M[;V])-M[;V])×COR
[13]  AVC←+/[2]((¯1 0)↓ M[;C]+1 ⊖ M[;C])÷200
[14]  'ENTER THE WEIGHT AND MOISTURE CONTENT OF THE COAL'
[15]  W←⌈/C←READ
[16]  MO←0.01× ⌊/C
[17]  'ENTER THE CARBON CONTET OF THE ASH RESIDUE'
[18]  FC←0.01×⍞
[19]  CDAF←(W×(1-MO))×FC
[20]  MM[;2]←+\FRACT÷CA←CDAF÷(+/FRACT←DLTVOL×AVC×12×4.2293E¯
2  )
[21]  MM[;3]←(1-(1-MM[;2])*÷3)×3
[22]  MM[;4]←-(⍟(1-MM[;2]))
[23]  MM[;1]←¯1 ↓ M[;1]
[24]  MM[;5]←MM[;1]÷HT←(⌽[2](1 1 0 0 0)/[2]MM) INTERPOLATE
      0.5
[25]  'ENTER TITLE'
[26]  TITLE←⍞
[27]  VECT←0 1 0
[28]  Z←CHOP/[1]MM
[29]  'PREPARE PRINTER'
[30]  C←⍞
[31]  TITLE
[32]  'THE TOTAL AMOUNT OF CARBON AT START OF GASIFICATION
';CA
[33]  'HALF TIME  ';HT
[34]  'TIME      X  3(1-(1-X)*÷3)  LN(1-X)  1/T'
[35]  Z
      ∇


      ∇ X←QUADFIT
[1]   X←Z[;2]⌹ Z[;1]∘ .*0 1
[2]   X←(X←Z[;3]⌹ Z[;1]∘ .*0 1),X
      ∇
```

```
      ∇ PLOT COL ;BLK;SCT;A
[1]   SECT←,SECT←(0 20 ⍴(1 + ⍴ M))
[2]   A←0
[3]  DLTA: → (SECT[1]<A=A+1)/ENDDLTA
[4]   BLK←(20×A-1)+⍳ 20
[5]   (2×M[BLK;1])PLOTCOORD M[BLK;COL]
[6]   → DLTA
[7]  ENDDLTA: BLK←(20×A -1)+⍳ SECT[2]
[8]   (2×M[BLK;1])PLOTCOORD M[BLK;COL]
      ∇


      ∇ Z←X PLOTCOORD Y
[1]   PX←(⌊/X)+0,(⍳ 100)×0.01×(⌈/X)-⌊/X
[2]   Z←PX,[1.5]PX SPLINEVAL X SPLINECALC Y
      ∇


      ∇ C←X SPLINECALC Y ;N;I
[1]   N←4×¯2+⍴ Y←0,Y
[2]   C←1 0 0 0 0 0 0 1 1 1 1 0 0 0 0 1 2 3 0 ¯1 0 0 0 2
      6 0 0 ¯2
[3]   C←((N-2 0)⍴(4+4×N)⍴(5,N)+ 4 7 ⍴ C),[1]¯1 2 ⌽ 0 7 ⍴ N +
 2 20
[4]   C←X,((⍴ X),4)⍴ Y[,I←1 ⌈(1 + ⍳⍴ X)∘ .+ 0 1,2 ⍴ -N]⊞ C
      ∇


      ∇ R←X SPLINEVAL C ;J
[1]   J←1 ⌈+/X ∘.>R←C[;1]
[2]   R←+/C[J;2 3 4 5]×((X-R[J])*((1 + R)- ¯1 + R)[J]) ○.*
      0 1 2 3
      ∇


      ∇ RUN
[1]   REFINE
[2]   RATE
      ∇


      ∇ Z←NO N
[1]   Z←24 60 ⍴(⌊ /T)+2+2×N
      ∇
```

```
    ∇ REFINE;T;SPAN;ZERO;C;N;TT;DIM
[1]   ∈')DIGITS 5'
[2]   DIM←⍴M←1 0↓(DATA∨.≠0)/[1]DATA
[3]   SPAN←ZERO←(¯2+¯1↑DIM)⍴0
[4]   'ENTER THE FINAL SPAN AND ZERO VALUE FOR  CO '
[5]   SPAN[2]←1-ICO↓(⌈/C)-ZERO[2]←(⌊/C←READ)
[6]   'ENTER THE FINAL SPAN AND ZERO VALUE FOR  CO2 '
[7]   SPAN[1]←1-ICO2↓(⌈/C)-ZERO[1]←(⌊/C←READ)
[8]   TT←(⌈/T)-⌊/(T←¯2↑,(1 3↑DATA))
[9]   →(2=⍴SPAN)/L1
[10]  'ENTER THE FINAL SPAN AND ZERO VALUE FOR  CH4 '
[11]  SPAN[3]←1-CH4↓(⌈/C)-ZERO[3]←(⌊/C←READ×2)
[12]  M[;4]←M[;4]×2
[13]  L1:DIM←1+⍳(⍴SPAN)
[14]  M[;DIM]←M[;DIM]-((N∘.×ZERO)+(N←(M[;1]←M[;1]×2)↓TT)∘.×SPAN)
    ∇
```